

Ultra-pure Cu obtaining using zone melting: influence of liquid zone width on impurities' behavior

UDC 669.2/8:669.3:669.049.44 **N. K. Dosmukhamedov**, Professor of a Chair "Metallurgy and Dressing of Mineral Resources"¹, e-mail: nurdos@bk.ru
E. E. Zholdasbay, Senior Researcher of a Chair "Metallurgy and Dressing of Mineral Resources"¹
G. B. Nurlan, Engineer of a Chair "Metallurgy and Dressing of Mineral Resources"¹

¹ Kazakh National Research Technical University named after K. I. Satpayev, Almaty, Kazakhstan.

In work with the use of a new precision design of the zone melting unit, which allows to regulate the main parameters of the process (width and velocity of the molten zone), technological experiments were carried out to obtain ultrapure copper, depending on the temperature distribution. Peculiarities of the behavior of impurity metals and the laws governing their distribution between the solid and liquid phases are established under conditions of a change in the width of the molten zone and high gradients of the temperature gradients 1183, 1233 and 1283 °C.

It has been found that the number of passes equal to four and the ratio of the width of the liquid zone (X) to the total length of the rod (L), $X/L = 0.15$, is sufficient conditions to achieve an ordered distribution of impurities along the rod within the entire range of temperature variation without the time of exposure to liquid zone. It is shown that the best results for the purification of copper from impurities are reached at a temperature of 1233 °C, exceeding the melting point of copper at 150 °C. The absolute decrease in the total concentration of impurity metals at this temperature was 371.68 ppm. The copper content in the final purified copper matrix corresponds to 5N3 (99.9993%).

On the basis of a change in the concentrations of impurity metals, the distribution coefficients of impurity metals were calculated in the range of reduction of the ratio with $X/L = 0.35$ to $X/L = 0.15$. The high values of the metal distribution coefficients at $X/L = 0.35$ and their decrease in the Co, Ni, Fe, Mn and As series are established: $K_{Co} = 8.0$; $K_{Ni} = 6.33$; $K_{Fe} = 4.4$; $K_{Mn} = 3.0$; $K_{As} = 1.0$. It is not possible to achieve deep copper purification from Co, Ni, Fe, Mn, B, and As in the production of ultrapure copper by zone melting. In this case, an increase in the copper content in the matrix of purified copper must be achieved by deeper cleaning of other impurity metals present in the initial copper to be purified.

It is established that the designed design of the plant allows to regulate a number of such important parameters of zone melting as the temperature of the molten zone, the spreading of the boundaries of the liquid zone, diffusion in the liquid zone by imposing a magnetic field. Flexible regulation of these parameters makes it possible to achieve deep segregation of volatile metal impurities even at sufficiently high values of the ratio $X/L = 0.35$.

It is shown that a sufficient degree of segregation for a number of volatile metal impurities (Pb, Bi, Ag, Sn, P, Sb, Zn) is observed at a ratio of $X/L = 0.35$ due to their high vapor pressure elasticity, compared to copper. A deeper degree of purification of copper from them is achieved at a ratio of $X/L = 0.15$. Moreover, in the range of reduction of the ratio with $X/L = 0.35$ to $X/L = 0.15$, their concentrations undergo slight changes.

It has been established that a decrease in the ratio X/L in the range from $X/L = 0.35$ to $X/L = 0.15$ significantly affects the change in the concentrations of impurity metals having a distribution coefficient $K > 1$ (Fe, Ni, Co, Mn, As). It is shown that the behavior of this group of impurity metals under conditions of high temperature of 1233 °C is associated with their interaction with each other and the formation of a number of chemical compounds that concentrate in the solid phase and create a convective flow that prevents the equipartition of each separately taken impurity from the liquid zone in solid phase. This phenomenon reduces the degree of purification of copper from this group of metals.

Key words: purification, zone melting, temperature, width of liquid zone, impurity, concentration, segregation, ultrapure copper.

DOI: 10.17580/nfm.2017.02.03

Introduction

Because of a low resistivity and high electromagnetic properties of Cu, its use as a substitute of Al and Al alloys in ultra-large-scale integral circuits, and an often reduction of sizes of microelectronic devices' elements, significantly drove up the demand for ultra-pure Cu [1–3].

Obtaining of ultra-pure Cu is complicated because of a strong affinity of some metallic and non-metallic impurities in Cu, as well as high values of vapor pressure and equilibrium of segregation coefficients, which are close to 1 for most impurity metals [4–7]. Many

investigators made an attempt to obtain an ultra-pure Cu with various methods of its purification from impurities. As an example, the study [8] shows an efficient method of Cu purification from Al, S, Cr, Ni, As, Se and Bi in chloride medium. The authors of the study [9] show a large separation of S, Se, Al and Si from Cu using the zone purification of Cu with floating liquid zone of Cu refining in hydrogen atmosphere. Significant vaporation of Zn, Sn, As, Bi, Cd, S and P was reached during the Cu refining by vacuum induction melting in the temperature range from 1356 to 1500 K [10]. However, all well-known processes of Cu refining have very typical complex

structure and low production capacity, which requires the choice of easily-mechanized and more efficient methods of Cu refining from impurities. One of such methods may be a zone purification of metals by zone melting. Scientific literature knows enough information about the successful application of this method for obtaining of various ultra-pure metals and alloys on their basis [11–16].

Our previous study [17] shows the design of a new fine adjustment of zone melting and gives the results of investigations of purification of Cu, containing a wide range of impurity metals (total concentration of impurities is 380 ppm). The investigations of the influence of the molten zone temperature and its holding time on the final grade of Cu purification from impurities defined the minimal content of impurities (9.8 ppm) in the final Cu matrix, reached with the molten zone temperature 1233 °C (higher than the Cu melting temperature by 150 °C) and its holding time 15 min.

The obtained positive results and wide functional possibilities of the designed zone melting unit allow the additional complex investigating for further deep removing of impurities from Cu with obtaining of ultra-pure Cu 5N.

The purpose of our study is investigation of the influence of the molten zone width on behavior of impurity metals during the zone purification of Cu and definition of optimal parameters, providing the minimization of the content of impurities in the final Cu matrix, which quality is similar to the one of the ultra-pure Cu 5N.

Methodology for investigations

Technological experiments were carried out using the zone melting unit, which design and operating principle are described in the study [17] in detail.

The Cu bars with Cu content of 99.96%, length of 800 mm and diameter of 30 mm were used as raw materials. These bars were used by remelting of cathode Cu M2k with the following composition, %: 99.94 Cu; 0.001 Bi; 0.002 As; 0.002 Sb; 0.002 P; 0.005 Pb; 0.002 Sn; 0.003 Ni; 0.005 Fe; 0.004 Zn; 0.003 Ag; 0.010 S.

Our experimental investigations concluded in the assessment of the change of concentrations of impurity metals in the final metal depending on the ratio of liquid zone width (X) to the bar length (L) with the given temperatures of the molten zone, exceeding the Cu melting temperature by 100, 150 and 200 °C.

Our experimental method was identical to the experimental conditions, described in the study [17] in detail. The difference was in the fact that Cu was purified from impurities with lesser quantity of runs (4 instead of 5) and different ratio of liquid zone width (X_i) to the bar length (L): 0.35; 0.25; 0.15.

Each investigation used various inductor heads, which provided the given width of the liquid zone. Spreading of the liquid zone boundaries was prevented by the magnetic field, created by using the magnetic rings. This field, in its turn, created the intense mixing of the liquid zone during the whole experiment, which provided the removing of

diffusion difficulties in it. For the purpose of increasing of production capacity of the unit, the experiments were carried out without the time of liquid zone holding.

Experimental results and their discussion

The Table shows the results of experiments for Cu purification from impurities using zone melting with various technological parameters.

The best results for Cu purification were reached at the temperature of 1233 °C over the whole range of the change of ratio of liquid zone width to the bar length. The ultra-pure Cu with high Cu content of 99.9993% was obtained at $X_i/L = 0.15$.

The dependence of the total content of impurity metals on the temperature of molten zone with the constant X_i/L is shown by quite complicated values (Fig. 1).

With the constant X_i/L , total concentration of impurity metals is decreased with temperature growth. At the same time, the defined regularity is very specific in the temperature range from 1183 to 1233 °C. At the temperature growth to 1283 °C, there is observed the smooth increase of the total concentration of impurity metals. At that, the defined regularity persists for all three temperatures, regardless of the change of the X_i/L . The similar values of the total concentration of impurities tell about the ordered distribution of impurities along the bar at high temperatures. If the increasing of temperature from 1183 to 1233 °C decreases the total concentration of impurities from 11.5 ppm to 4.5 ppm with constant $X_i/L=0.15$, the further growth of temperature to 1283 °C will increase the total concentration of impurities to 7.5 ppm at the constant $X_i/L = 0.15$.

A smooth increase of total concentration of impurity metals at high temperatures is caused by the redistribution of impurity metals between liquid and solid phases, and formation of chemical compounds of impurity metals with each other.

The Fig. 2 shows the dependence of the change of total concentration of impurity metals on the change of the ratio of the molten zone width to the bar length at fixed temperatures exceeding the Cu melting temperature by 100, 150 and 200 °C.

For all the investigated temperatures, the total content of impurity metals in the final Cu is decreased with the

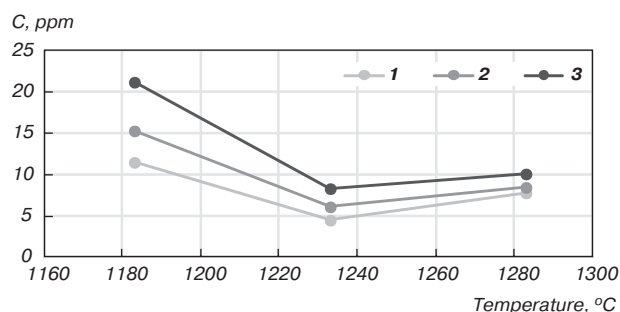


Fig. 1. Dependence of total concentration of impurity metals on temperature at X/L : 1 – 0.15; 2 – 0.25; 3 – 0.35

The conditions and results of technological experiments on Cu purification from impurities

| Impurity metals | Initial concentration, C_0 , ppm | Content of impurities, C_i , ppm | | | | | | | | |
|----------------------------------|------------------------------------|------------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| | | 1183 °C | | | 1233 °C | | | 1283 °C | | |
| | | $X/L = 0.35$ | $X/L = 0.25$ | $X/L = 0.15$ | $X/L = 0.35$ | $X/L = 0.25$ | $X/L = 0.15$ | $X/L = 0.35$ | $X/L = 0.25$ | $X/L = 0.15$ |
| Pb | 50 | 1.1 | 0.5 | 0.25 | 0.25 | 0.1 | 0.02 | 0.2 | 0.2 | – |
| Bi | 20 | 0.9 | 0.6 | 0.12 | 0.1 | 0.09 | 0.07 | 0.1 | 0.1 | – |
| Fe | 50 | 3.7 | 3.3 | 3.1 | 2.2 | 1.7 | 1.3 | 2.8 | 2.8 | 2.9 |
| Cr | 30 | 1.5 | 0.6 | 0.13 | 0.2 | 0.15 | 0.1 | 0.1 | 0.1 | 0.02 |
| Mn | 30 | 1.9 | 1.5 | 1.3 | 0.9 | 0.6 | 0.4 | 1.5 | 0.5 | 0.9 |
| Ni | 30 | 3.1 | 2.8 | 2.6 | 1.9 | 1.3 | 1.1 | 2.4 | 1.8 | 1.9 |
| Zn | 40 | 0.8 | 0.4 | 0.15 | 0.11 | 0.03 | 0.007 | 0.1 | 0.1 | 0.1 |
| Ag | 30 | 0.8 | 0.5 | 0.11 | 0.13 | 0.04 | 0.006 | 0.1 | 0.1 | 0.1 |
| Co | 20 | 2.7 | 2.5 | 2.2 | 1.6 | 1.2 | 0.9 | 1.6 | 1.57 | 1.65 |
| Sb | 20 | 0.9 | 0.6 | 0.11 | 0.09 | 0.07 | 0.06 | 0.1 | 0.1 | 0.1 |
| As | 20 | 1.2 | 0.7 | 0.4 | 0.29 | 0.22 | 0.2 | 0.3 | 0.2 | – |
| Sn | 20 | 0.8 | 0.3 | 0.12 | 0.1 | 0.02 | 0.006 | 0.1 | 0.1 | 0.03 |
| P | 20 | 0.9 | 0.5 | 0.11 | 0.2 | 0.09 | 0.004 | 0.1 | 0.1 | 0.02 |
| B | 10 | 0.9 | 0.5 | 0.8 | 0.6 | 0.5 | 0.3 | 0.6 | 0.7 | 0.08 |
| Total content of impurities, ppm | 380 | 21.2 | 15.3 | 11.5 | 8.32 | 6.11 | 4.5 | 10.1 | 8.47 | 7.8 |
| Cu content | 99.96 | 99.991 | 99.9923 | 99.993 | 99.9982 | 99.999 | 99.9993 | 99.9943 | 99.9963 | 99.9978 |

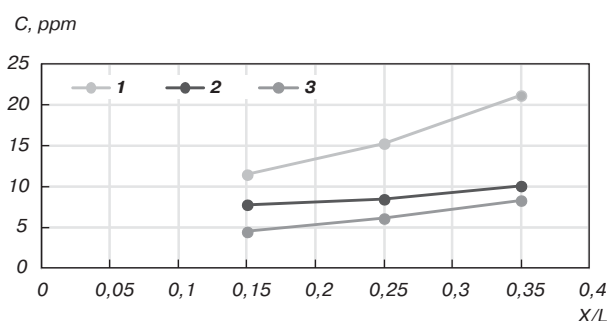


Fig. 2. Dependence of change of total concentration of impurity metals (C) on ratio of liquid zone width (X) to bar length (L) at the temperatures of T :
1 – 1183 °C; 2 – 1233 °C; 3 – 1283 °C

reduction of X/L . At that, decreasing of the total content of impurities at high temperatures is more specific than the one at the temperature of 1183 °C.

The similar values of the obtained dependences for the fixed high temperatures (1233, 1283 °C) confirm the ordered distribution of impurity metals in the considered range of a change of ratio of the molten zone width to the bar length. At the constant temperature of 1233 °C, exceeding the Cu melting temperature by 150 °C, the sharp decrease of the total content of impurity metals is observed: from 380 to 8.32 and 4.5 ppm, respectively (Fig. 2), within the decrease of the ratio from $X/L = 0.35$ to $X/L = 0.15$.

The tendency of a sharp decrease of the total concentration of impurities continues at the temperature of 1283 °C either, which exceeds the Cu melting temperature by 200 °C: the total concentration of impurity metals is decreased from 380 to 10.1 and 7.8 ppm, respectively, within the decrease of the ratio from $X/L = 0.35$ to $X/L = 0.15$.

The dependence of the change of concentrations of impurity metals on the ratio of the molten zone width to

the bar length at the optimal temperature of 1233 °C is shown in the Fig. 3.

The defined regularities allow the mapping of the distribution of impurities along the refined ingot and defining their behavior during the change of the width of liquid zone on the basis of estimated distribution coefficients.

The impurity distribution coefficient is estimated on the basis of the concentration change results and the following formula: $K_{Me} = C_0/C_1$, where C_0 is the initial impurity concentration and C_i is the final impurity concentration.

Dependence of estimated values of impurity distribution coefficient (K_{Me}) on the X/L at the optimal temperature of 1233 °C is shown in the Fig. 4.

Distribution coefficients for impurity metals K_{Me} Ag, Zn, Pb, Sn are less than 1 and have low values. Having the $X/L = 0.35$, the impurity distribution coefficients are decreased in the range of Pb, Sn, Ag, Zn and have the following content: $K_{Pb} = 0.5$; $K_{Sn} = 0.5$; $K_{Ag} = 0.43$; $K_{Zn} = 0.28$ (Fig. 4, a). Distribution coefficients for these metals are decreased over the whole range of reduction of the ratio from $X/L = 0.35$ to $X/L = 0.15$. At the same time, with $X/L = 0.15$, the values of distribution coefficients of impurity metals move close to each other and reach their minimum at $K_{Me} = 0.02$, which is rather usual. In the conditions of Cu purification with zone melting at the constant temperature of 1233 °C and $X/L = 0.15$, the residual concentrations of impurity metals of this group, concentrating in the purified Cu, have rather low values (Table).

Distribution coefficients for Sb, Bi and Cr are within the range of $K_{Me} < 1$. Only As, belonging to these impurity metals too, has the distribution coefficient of more than 1 (Fig. 4, b). As well as in the previous case, metal distribution coefficients are decreased over the whole range of decreasing of X/L . At that, the values of distribution

coefficients of Sb, Bi and Cr within the reduction of ratio from $X/L = 0.35$ to $X/L = 0.15$ slightly increase the values of distribution coefficients for lead, tin, silver and zinc.

Distribution coefficients for Sb, Bi and Cr reach their minimums at $X_i/L = 0.15$ and have the following values: $K_{Sb} = 0.3$; $K_{Bi} = 0.35$; $K_{Cr} = 0.33$. The defined low values of distribution coefficients for Sb, Bi and Cr show their rather high separation from Cu: the residual concentrations of Sb, Bi and Cr in Cu, obtained after refining are 0.06, 0.07 and 0.1 ppm, respectively.

The behavior of As is quite different. In spite of an insignificant decrease of distribution coefficient from $K_{As} = 1.45$ to $K_{As} = 1.0$ at reduction X/L from $X/L = 0.35$ to $X/L = 0.15$, the As distribution coefficient stays rather high $K_{As} > 1$ over the whole range of change of X/L . This fact tells about a complex separation of As and Cu.

High values of distribution coefficients are defined for the impurity metals, placed in the VIII group of the periodic table: Fe, Ni, Co and Mn (Fig. 4, b).

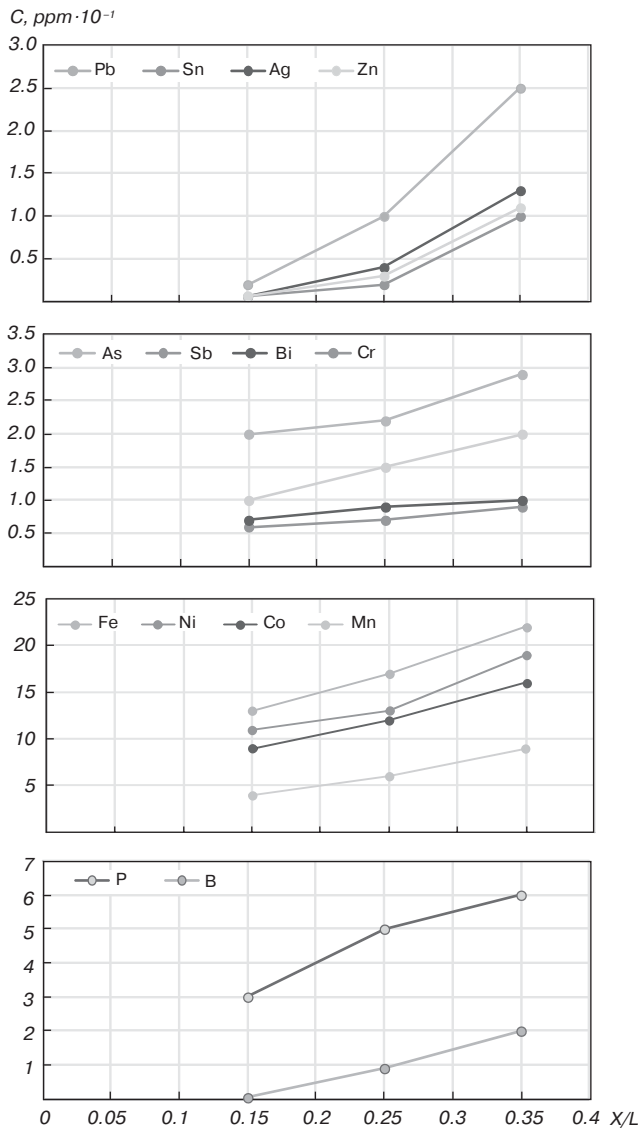


Fig. 3. Dependence of change of impurity metal concentrations on X/L at the temperature of $T = 1233$ °C

The Fig. 4, b shows that, depending on the decrease of ratio from $X/L = 0.35$ to $X/L = 0.15$ for all considered metals, the change of metal distribution coefficients is described by the identical nature of curves. Decreasing of metal distribution coefficients at the $X/L = 0.35$ is in the range of Co, Ni, Fe and Mn and has the following values: $K_{Co} = 8.0$; $K_{Ni} = 6.33$; $K_{Fe} = 4.4$; $K_{Mn} = 3.0$.

The minimal values of distribution coefficients of this group metals are reached at the ratio of $X_i/L = 0.15$: $K_{Co} = 4.5$; $K_{Ni} = 3.67$; $K_{Fe} = 2.6$; $K_{Mn} = 1.33$.

High residual concentrations of Co, Ni, Fe and Mn in refined Cu (0.9, 1.1, 1.3 and 0.4 ppm, respectively), as well as their high values of distribution coefficients, defined for the optimal condition of $X/L = 0.15$ show the difficulty of Cu purification from this group metals at the zone melting. This is explained by the formation of new stable chemical compounds in liquid phase as a result of interaction of Co, Ni, Fe, Mn with each other and with other impurity metals in liquid phase, which, with the following decrease

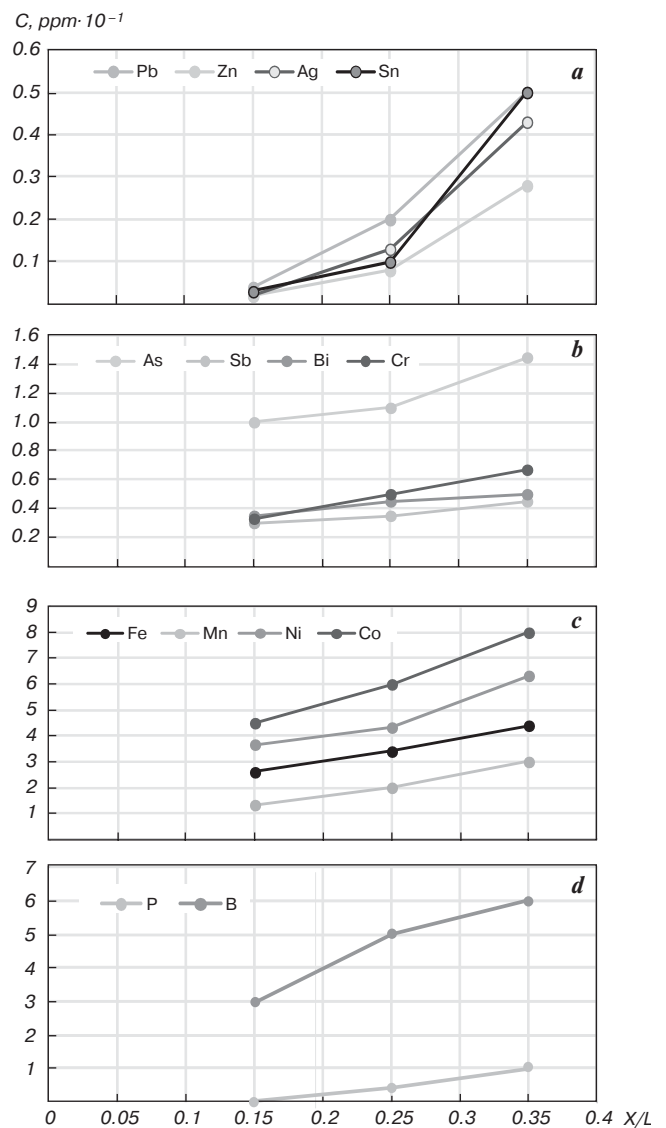


Fig. 4. Dependence of admixture distribution coefficients on X/L at the temperature of $T = 1233$ °C

of temperature are concentrated in the solid phase. At that, Fe intermetallides, dissolving a part of Ni, Co and Mn are formed as a result of interaction of Fe with As and Sb in the conditions of high temperatures in the liquid phase and are concentrated in the area of low temperatures in solid phase. The chemical compounds, formed in the solid phase, create a front convective flow, which resists the equal transfer of impurities back from the molten zone. As a result of the defined mechanism, the concentrations of Fe, As, Sb, Ni, Co and Mn are highly decreased, which is confirmed by the experimental results. This supposition is completely approved by the constitutional diagram Fe – As and Fe – Sb.

Dependence of estimated values of B and F distribution coefficient on the X/L (Fig. 4, *d*) show the impossibility of rather deep removing of B in experimental conditions. The maximal (in two times) decrease of B distribution coefficient from $K_B = 6.0$ to $K_B = 3.0$ is reached with $X/L = 0.15$.

A sharp decrease of P distribution coefficient from $K_P = 1.0$ ($X/L = 0.35$) to $K_P = 0.02$ ($X/L = 0.15$) supposes that rather deep segregation of P from Cu may be reached in the conditions of minimal X/L .

According to this, results of the carried out investigations of the peculiarities of behavior of impurity metals in the conditions of Cu purification by zone melting at the temperatures of 1183; 1233 and 1283 °C and X_i/L equal to 0.35; 0.25 and 0.15 show the principal possibility of obtaining of ultra-pure Cu_5N_3 (99.9993) at the optimal temperature of 1233 °C and $X/L = 0.15$.

The developed technology of Cu purification from impurity metals by zone melting may be used for obtaining of ultra-pure Cu from refined Cu with Cu content of not less than 99.9% (3N and more). Application of this technology is very urgent for purification of refined Cu M1k, obtained at the enterprises of Kazakhstan (LLC “Kazakhmys Corporation”, LLC “Kazzinc” and LLC “Casting”) where refined Cu is produced from secondary Cu raw materials with 99.9–99.97% of Cu. Quantity and content of impurity metals in refined Cu obtained at the enterprises of Kazakhstan share the whole spectrum of impurity metals which behavior was investigated in this study.

Conclusions

1. We defined the influence of the width of liquid zone on behavior of impurity metals at the temperatures of 1183, 1233 and 1283 °C at the obtaining of ultra-pure Cu by zone melting. Reaching of deep purification of Cu from Co, Ni, F, Mn, B and As at zone melting is not possible because of the defined high values of the metals distribution coefficients at the $X/L = 0.35$: $K_{\text{Co}} = 8.0$; $K_{\text{Ni}} = 6.33$; $K_{\text{Fe}} = 4.4$; $K_{\text{Mn}} = 3.0$; $K_{\text{As}} = 1.0$.

2. The optimal temperature of 1233 °C in the range of decreasing of the ratio from $X/L = 0.35$ to $X/L = 0.15$ shows the maximum segregation of Pb, Sn, Ag, Zn due to the high elasticity of vapors. Values of their distribution coefficients reach almost the same minimum equal to 0.02 at $X/L = 0.15$.

3. The optimal temperature of 1233 °C and $X/L = 0.15$ reach the best segregation conditions for Cr, Bi, Sb. This is explained by the sharp decrease of their distribution coefficients to the minimal values from $K_{\text{Cr}} = 0.67$; $K_{\text{Bi}} = 0.48$; $K_{\text{Sb}} = 0.42$ to $K_{\text{Cr}} = 0.1$; $K_{\text{Bi}} = 0.07$; $K_{\text{Sb}} = 0.06$.

References

1. Steigerwald J. M., Murarka S. P., Gutmann R. J. Chemical Mechanical Planarization of Microelectronic Materials. New York, John Wiley & Sons., 1997.
2. Torres J. Advanced Cu interconnections for Si CMOS technologies. *Applied Surface Science*. 1995. Vol. 91. p. 112.
3. Woo T.-G., Park I.-S., Seol K.-W. Effect of ion-beam assisted deposition on resistivity and crystallographic structure of Cr/Cu. *Electronic Materials Letters*. 2009. Vol. 5. pp. 105–107.
4. Kurosaka A., Tanabe N., Kohno O., Osanai H. *Proceedings of the 1st International Conference of Ultra High Purity Base Metals (UHPM-94)*. 1994. p. 446. Kitakyushu, Japan.
5. Dost S., Liu Y. C., Haas J., Roszmann J., Grenier S., Audet N. Effect of applied electric current on impurity transport in zone refining. *Journal of Crystal Growth*. 2007. Vol. 307, No. 1. pp. 211–218.
6. Cheung, T., Cheung N., Garcia A. Application of an artificial intelligence technique to improve purification in the zone refining process. *Journal of Electronic Materials*. 2010. Vol. 39 (1). pp. 49–55.
7. Zhu Y., Mimura K., Ishikawa Y., Isshiki M. Effect of Floating Zone Refining under Reduced Hydrogen Pressure on Cu Purification. *Materials Transactions*. 2002. Vol. 43, No 11. pp. 2802–2807.
8. Lalev G. M., Lim J.-W., Munirathnam N. R., Choi G.-S., Uchikoshi M., Mimura K., Isshiki M. Impurity Behavior in Cu Refined by Ar Plasma-Arc Zone Melting. *Metals and Materials International*. 2009. Vol. 15, No. 5. pp. 753–757.
9. Zhu Y., Mimura K., Ishikawa Y., Isshiki M. Effect of Floating Zone Refining under Reduced Hydrogen Pressure on Cu Purification. *Materials Transactions*. 2002. Vol. 43, No 11. pp. 2802–2807.
10. Yoon Y. O., Jo H. H., Cho H., Kim S. K., Kim Y. J. Effect of distribution coefficient in Cu purification by zone refining process. *Materials Science Forum*. 2004. Vol. 449–452. pp. 173–176.
11. Lim J.-W., Kim M. S., Munirathnam N. R., Le M. T., Uchikoshi M., Mimura K., Isshiki M., Kwon H. C. Choi G. S. Effect of Ar/Ar-H₂ Plasma Arc Melting on Cu Purification. *Materials Transactions*. 2008. Vol. 49, No. 8. pp. 1826–1829.
12. Cheung T., Cheung N., Tobar C. M. T., Caram R., Garcia A. Application of a Genetic Algorithm to Optimize Purification in the Zone Refining Process. *Materials and Manufacturing Processes*. 2011. Vol. 26. pp. 493–500.
13. Ghosh K., Mani V. N. and Dhar S. A modeling approach for the purification of group III metals (Ga and In) by zone refining. *Journal of Applied Physics*. 2008. pp. 104–112.
14. Dosmukhamedov N. K., Zholdasbay E. E. Optimization of the width and speed of molten zone in the conditions of purifying Cu of impurities by zone melting. *Austrian Journal of Technical and Natural Sciences*. 2016. No. 3–4. Section 3. Materials Science. pp. 20–22.
15. Alieva Z. U., Trubitsyn Yu. V. Aspects of control of kinetics of vertical float zone melting during the Si purification. *Novye materialy v metallurgii i mashinoborudovanii*. 2011. No. 1. pp. 106–110.

16. Liu D., Engelhardt H., Li X., Löffler A., Rettenmayr M. Growth of an oriented $\text{Bi}_{40-x}\text{In}_x\text{Te}_{60}$ ($x = 3,7$) thermoelectric material by seeding zone melting for the enhancement of chemical homogeneity. *CrystEngComm*. 2015. Vol. 17. pp. 3076–3081.

17. Dosmukhamedov N. K., Zholdasbay E. E., Nurlan G. B., Kurmanseitov M. B. Employment of zone melting to obtain ultrapure Cu: behavioural patterns of impurity metals. *Tsvetnyye Metally*. 2017. No. 7. pp. 34–41.

NFM

Remediation in conditions of an operating copper-nickel plant: results of perennial experiment

UDC 504.064+669.3+669.24

M. V. Slukovskaya, Senior Researcher¹, e-mail: krem.mv@gmail.com

I. P. Kremenetskaya, Senior Researcher¹

L. A. Ivanova, Head of Laboratory²

T. N. Vasilieva, Senior Researcher¹

¹ I. V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, Kola Science Center of the Russian Academy of Sciences, Apatity, Russia.

² N. A. Avrorin Polar-Alpine Botanical Garden-Institute, Kola Science Center of the Russian Academy of Sciences, Apatity, Russia.

The paper presents the results of a long-term experiment on remediation of depressed territories (technogenic barrens) in Subarctic (the Kola Peninsula, Russia). The main negative factors, hampering processes of natural restorative succession of such territories, are the inclement environmental conditions and permanent aerotechnogenic exposure, which leads to high acidity level and high concentrations of metals in atmospheric precipitation and soil solutions.

An innovative “mild” remediation technique of soils in an impact zone of a copper-nickel plant, using different types of mining wastes, has been put forward. It has been shown that these wastes serve as effective ameliorants due to high content of calcium and magnesium carbonates and/or silicates and have a prolonged beneficial effect on nutrient regime of soils. The vegetable cover of grain crops established on the above mentioned wastes without resorting to soil and peat, scarce in the region, has been proven to be productive and resistant to aerotechnogenic burden.

In order to estimate favorability of technosoil during the process of monitoring research of artificial phytocenosis evolution, there has been suggested an integral index — module of toxicity, defined as a ratio of phytoavailable copper and nickel aggregate content to calcium and magnesium, expressed in mole units. It has been found that sungulite wastes of phlogopite mining (city of Kovdor, Murmansk region) appear to be a sort of mining wastes which have considerable promise with relation to effectiveness of land-improvement and economic expediency of their use in large-scale work on remediation of depressed territories in subarctic conditions.

Key words: remediation, grass, industrial barren, mining waste, Subarctic, copper-nickel plant, aerotechnogenic exposure, impact zone, ameliorant, pollutant, state of ecosystem, toxicity module.

DOI: 10.17580/nfm.2017.02.04

Introduction

Operating enterprises of non-ferrous metallurgy exert an adverse effect on environment mainly by pollutant emission into atmosphere with their consequent falling over adjacent territories, which leads to pollution of all vital environments and degradation of ecosystems [1, 2]. In the impact zones of large-scale enterprises, technogenic barrens may arise. These are the open landscapes with contaminated and eroded soils, completely or almost completely (>90%) lacking in vegetation [2]. Arising of 36 technogenic barrens were observed in the world, most of which are situated in northern hemisphere (Central Europe, USA and Russia) [2, 3].

At present, the plant biomass in an impact zone of the copper-nickel plant near the city of Monchegorsk (Murmansk region, Russia) forms 1% of biomass of uncontaminated forests, which is connected with emissions of heavy metals

and sulfur dioxide [3]. Conflagrations, disafforestations, harmful activity of destructive insects, changes in moisture nature of the territory introduce an additional contribution into digression of ecosystems [3, 4].

The limiting factors of recovering the growth on technogenic barrens of the Kola Peninsula are such soil parameters as extreme copper and nickel concentrations, shortage of nutrient elements (K, Ca, Mg, P, Mn), high acidity, low moisture as well as scanty seed bank and lack of plant renewal underground organs [4, 5]. Progressive successions in the impact zone on this territory are impossible without human intervention even after termination of the plant operation [6]. At present, as aerotechnogenic emissions of the Kola Mining and Metallurgical company JSC are decreasing in comparison with the level of 1990-ies, secondary pollution owing to erosion of soils and migration of heavy metals have a pronounced effect on ecological situation [7, 8]. In this