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Hydrometallurgical refining of metallurgical silicon

N. V. Nemchinova ✉, **A. A. Tyutrin, A. A. Zaitseva**

Irkutsk National Research Technical University (83 Lermontova Str., Irkutsk 664074, Russian Federation)

ninavn@yandex.ru

Abstract. The paper presents the results of refining silicon of metallurgical grades based on leaching of impurities with inorganic acids. Silicon samples were studied by metallographic and *X*-ray fluorescent methods of analysis, as well as *X*-ray spectral microanalysis. To improve the quality of this alloying element, we carried out experimental work on its hydrometallurgical purification with solutions of various acids (10 % H_2SO_4, HCl, HNO_3, 4 % HF) and their mixtures. Values of changes in the Gibbs energy were calculated for reactions of interaction with reagents of the main impurity inclusions recorded in the studied silicon samples ($FeSi_2$, Fe_2Si, FeSi, AlFeSi, $AlFeSi_2$, Al_3FeSi_2, $FeSi_2Ti$, FeAlTiSi, $TiSi_2$, Ca_2Si). The experiments were carried out on silicon samples with a particle size of –200 μm with constant stirring by a magnetic stirrer at a temperature of 60 °C, duration 1 h and L:S = 5:1. Determination of concentration of the impurity elements in the solution after leaching was made by the atomic emission method of analysis. When hydrofluoric acid is used as a solvent, the best results are obtained for purification of iron, aluminum, and titanium (concentration in solution, mg/dm^3, respectively: 2380, 831, 145). The maximum concentration of calcium in the solution (147 mg/dm^3) was achieved by hydrochloric acid treatment of fine silicon. The most effective for transferring impurities into solution is a mixture of sulfuric and hydrofluoric acids at a ratio of 1:1. Using a mixture of H_2SO_4 and HCl as a solvent (at a ratio of 1:3) made it possible to achieve sufficiently high mass concentrations of impurity elements in the leaching solution. The degree of silicon purification from iron was 33.32 %, aluminum – 54.64 %, calcium – 65.77 %, titanium – 15.64 %.

Keywords: technical (metallurgical) silicon, impurities, hydrometallurgical refining, Gibbs energy change

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Гидрометаллургическое рафинирование металлургического кремния

Н. В. Немчинова ✉, **А. А. Тютрин, А. А. Зайцева**

Иркутский национальный исследовательский технический университет (Россия, 664074, Иркутск, ул. Лермонтова, 83)

ninavn@yandex.ru

Аннотация. Приведены результаты рафинирования кремния металлургических марок на основе выщелачивания примесей неорганическими кислотами. Образцы кремния как объекты исследований изучаются металлографическим, рентгенофлюоресцентным методами, а также рентгеноспектральным микроанализом. Для повышения качества кремния были проведены экспериментальные работы по его гидрометаллургической очистке растворами различных кислот (10 %-ными H_2SO_4, HCl, HNO_3; 4 %-ной HF) и их смесями. Рассчитаны изменения энергии Гиббса для реакций взаимодействия с реагентами основных примесных включений, зафиксированных в исследуемых образцах кремния ($FeSi_2$, Fe_2Si, FeSi, AlFeSi, $AlFeSi_2$, Al_3FeSi_2, $FeSi_2Ti$, FeAlTiSi, $TiSi_2$, Ca_2Si). Эксперименты проводились на пробах кремния крупностью частиц –200 мкм при постоянном перемешивании магнитной мешалкой при температуре 60 °С, продолжительности 1 ч и соотношении Ж:Т = 5:1. Определение концентрации примесных элементов в растворе после выщелачивания проводили атомно-эмиссионным методом. Установлено, что при использовании в качестве растворителя плавиковой кислоты получены наилучшие результаты по очистке от железа, алюминия, титана (концентрация в растворе 2380, 831, 145 мг/дм^3). Максимальная концентрация кальция в растворе (147 мг/дм^3) достигается при солянокислой обработке мелкофракционного кремния. Наиболее эффективной для перевода примесей в раствор является смесь серной и плавиковой кислот при их соотношении 1:1. Использование в качестве растворителя смеси H_2SO_4 и HCl (при соотношении 1:3) позволяет достигать достаточно высоких массовых концентраций примесных элементов в растворе выщелачивания. Степень очистки кремния от железа составляет 33,32 %, алюминия – 54,64 %, кальция – 65,77 %, титана – 15,64 %.

Ключевые слова: технический (металлургический) кремний, примеси, гидрометаллургическое рафинирование, изменение энергии Гиббса

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Introduction

Technical (metallurgical) silicon finds widespread application globally in various fields [1]. It is utilized as an alloying element in ferrosilicon and high-silicon alloys [2 – 4], as an alloy in the aluminum industry to produce silumins [5], as a steel deoxidizer in the steel industry [6], and in the chemical industry to obtain organosilanes and other compounds [1; 4]. In the electronics industry, high-purity semiconductor silicon and silicon of "solar" quality serve as the basis for photoelectric current converters [4; 6].

Metallurgical silicon produced by melting in ore thermal furnaces [5; 7 – 9] typically has a purity of only 98.0 – 99.5 %. At present, "solar" quality silicon is manufactured by combining the costly "electronic" silicon and metallurgical silicon, followed by refining through crystallization methods. The Siemens process [10] is the traditional industrial method of producing "electronic" silicon, along with other similar methods that involve vapor phase chemical precipitation for the production of chlorosilane compounds. However, these methods have drawbacks such as high volatility, toxicity, and equipment corrosion in the presence of water. The Siemens process is also highly energy-intensive, consuming approximately 120 kWh/kg of silicon [11]. Alternatively, "solar" quality silicon can be obtained by processing metallurgical silicon, which can involve oxidative refining [5; 12; 13], hydrometallurgical purification [5; 14; 15], vacuum refining [16 – 18], and crystallization methods of purification (direct crystallization, zone melting) [19 – 22]. Of these methods, hydrometallurgical refining is the only process that does not require high temperatures (below 100 °C) or expensive equipment. This method is energy-efficient and cost-effective.

The objective of this study is to conduct experiments for hydrometallurgical purification of metallurgical silicon using various inorganic acids.

Subject of research

The aim of this study was to investigate metallurgical silicon samples obtained from Silicon JSC, RUSAL (Shelekhov, Irkutsk Region) after undergoing oxidative refining.

Technical silicon is typically produced through a continuous method in ore-thermal furnaces (OTF) using silica-containing raw materials with a minimum of 98.5 % SiO_2. Fossil quartzite is a mineral component commonly used in charge mixtures for industrial processes. The mixture typically includes a combination of carbon reducing agents such as charcoal, petroleum coke, and hard coal from various producers such as Kazakhstan and Colombia. Additionally, wood chips are often used as a charge loosener [5; 7].

The process of silicon smelting can be generally described by the reaction $SiO_2 + 2C = Si + 2CO$. However, this oversimplified reaction does not adequately capture the complexity of the reduction of silica that occurs in a furnace during silicon production. In an OTF, silicon production is a highly intricate, high-temperature process that involves various chemical reactions resulting in the formation of intermediate compounds such as SiO and SiC.

The raw materials used for silicon production, such as Cheremshansk Mine quartzite, exhibit heterogeneity in terms of impurity content. As a result, the resulting smelted silicon contains small amounts of iron, calcium, aluminum, and titanium, which give rise to the formation of various intermetallic inclusions within the silicon [23; 24].

At Silicon JSC, the process of silicon production involves the smelting of the charge in an OTF, followed by an oxidative refining step in which air blowing is used to remove mainly aluminum and calcium from the silicon melt [7]. However, this method does not remove iron from the silicon, which highlights the importance of strict control over the supply of iron from the charge materials (quartzite, carbonaceous reducing agents). Alternatively, other methods may be suggested to improve the quality of silicon.

Different methods were employed to study the chemical composition of technical silicon samples used in experimental works.

Different methods were employed to study the chemical composition of technical silicon samples used in experimental works. Metallographic studies of thin sections of the initial lump silicon revealed the presence of mainly impurity intermetallic inclusions (Fig. 1). This study was conducted using an Olympus GX-51 metallographic microscope (Olympus, Japan) equipped with an Altera20 digital camera. Additionally, *X*-ray spectral microanalysis (Fig. 2) was performed using an S4 Pioneer *X*-ray spectrometer (Bruker, Germany). The results indicated that iron and aluminum were the main impurity components of intermetallic inclusions present in the silicon sample, albeit in insignificant amounts.

The initial lump material was crushed using by a ShchD-10 jaw crusher (Russia), and subsequently ground using a ShM-1408 ball mill (Russia). The grinding process employed steel balls without lining, and magnetic separation was then applied. The particle-size distribution of the resulting fine silicon was analyzed using a laser particle size analyzer, Analyzette 22 NanoTecPlus (FRITSCH, Germany). The iron impurity is present in small inclusions (Fig. 2), resulting in a uniform distribution by fractions. The results of the analysis are presented in Fig. 3 and in the Table.

Based on the particle-size analysis, it was found that the metallurgical silicon particles had a frac-

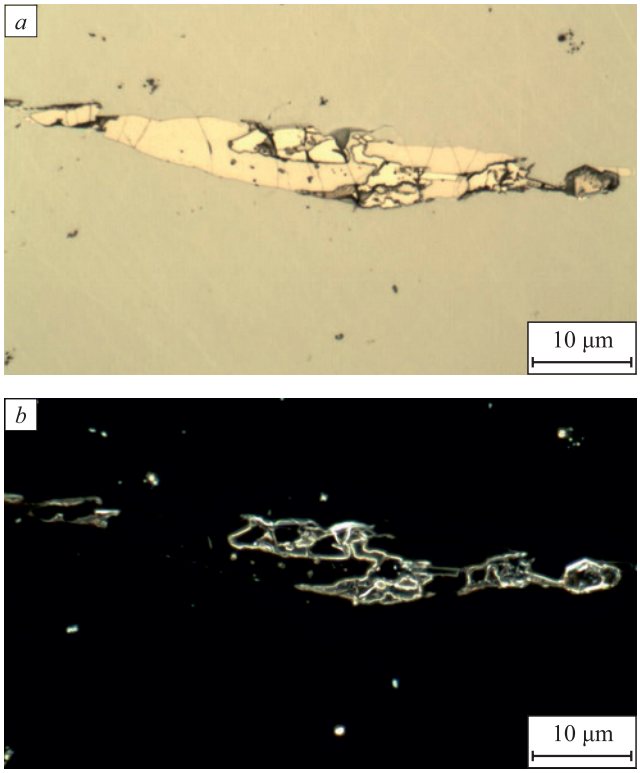

Fig. 1. Inclusions of intermetallides in a silicon sample:
a and *b* – light and dark field

Рис. 1. Включения интерметаллидов в образце кремния:
a и *b* – светлое и темное поле

tion size of –200 μm; with 80 % of all particles falling within the fraction size range of +12 ÷ 100 μm. Elemental chemical composition (wt. %) of the material was determined through *X*-ray fluorescent analysis (XRF), which resulted in the following values (wt. %): Al 0.53; Ti 0.0491; Ca 0.0628; V 0.0066; Cr 0.0024; Mn 0.0145; Fe 0.6094; Cu 0.0037; P 0.0106; Ba 0.0077; Ni 0.0071; Zn 0.0022 and Si 98.6939 (taking into account 12 impurities). The XRF analysis was conducted using an S4 Pioneer *X*-ray spectrometer.

The XRF spectra of the technical silicon samples after oxidative refining (Fig. 4) indicated the presence of various impurity elements such as iron, titanium, aluminum, and calcium. Iron was the most prevalent impurity, and is notoriously difficult to remove through flux-oxygen refining of silicon, primarily due to its low affinity to oxygen. As a result, iron remains almost entirely within the silicon melt and does not transfer to slag.

Experimental work on hydrometallurgical purification of silicon

The quality of technical silicon was attempted to be improved by using solutions of sulfuric, nitric, hydrochloric, and hydrofluoric acids, as well as their mixtures in different proportions as reagents for silicon processing. To assess the potential of these solvents in hydrometallurgical refining, changes in Gibbs energy (ΔG°_{298}) were calculated as an indicator of the thermodynamic likelihood of chemical interactions between impurity inclusions (intermetallics) and various solvents.

Iron impurities in silicon can exist in various forms such as double silicides including ($FeSi_2$, Fe_2Si, FeSi) and in complex intermetallic compounds containing titanium and/or aluminum including (AlFeSi, $AlFeSi_2$, FeTiSi, $FeTiSi_2$, $FeAl_3Si_2$, FeAlTiSi) [23 – 25]. The interaction of FeSiTi intermetallic with a sulfuric acid solution can be described by the following reaction

$$2\,FeSiTi + 7\,H_2SO_4 + 6\,H_2O =$$
$$= Fe_2(SO_4)_3 + 2\,Ti(SO_4)_2 + 2\,H_2SiO_3 + 11\,H_2$$

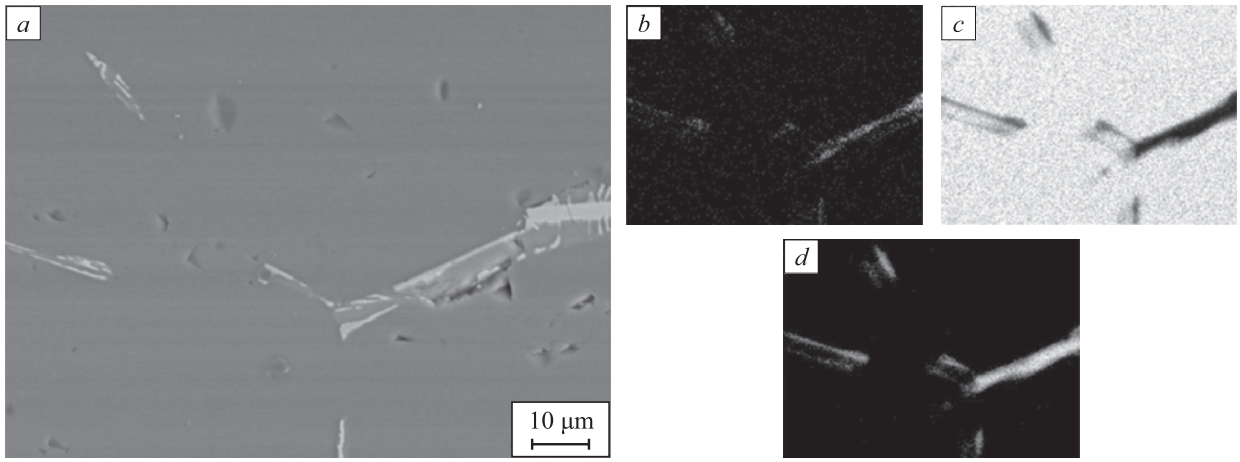

Fig. 2. Results of *X*-ray spectral microanalysis of metallurgical silicon samples (*a*)
with determination of the area of iron (*b*), silicon (*c*) and aluminum (*d*)

Рис. 2. Результаты рентгеноспектрального микроанализа образцов металлургического кремния (*a*)
с определением области нахождения железа (*b*), кремния (*c*) и алюминия (*d*)

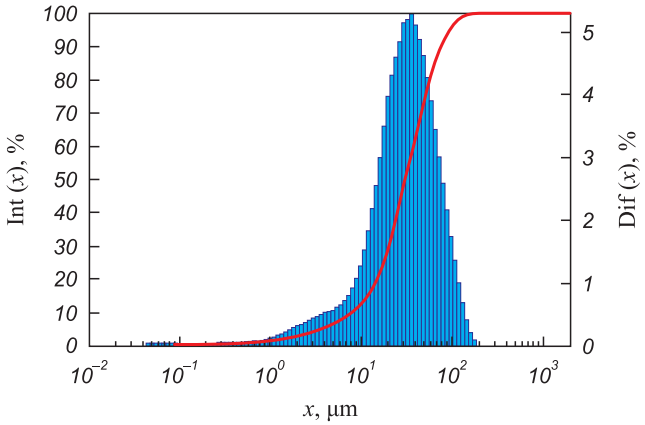

Fig. 3. Particles size distribution in a sample of metallurgical silicon

Рис. 3. Распределение частиц пробы металлургического кремния по крупности

the ΔG°_{298} value is –2412.34 kJ/mol, indicating a spontaneous process.

A software program was developed in Microsoft Excel for the rapid calculation of the ΔG°_{298} values of chemical reactions [26]. The program was used to determine the ΔG°_{298} values for the interactions of various compounds, including $FeSi_2$, Fe_2Si, FeSi, AlFeSi, $AlFeSi_2$, Al_3FeSi_2, $FeSi_2Ti$, FeAlTiSi, $TiSi_2$ and Ca_2Si with solutions of different acids. The calculated ΔG°_{298} values were found to be negative [27].

In order to conduct the experiments, silicon samples with a particle size of –200 μm were obtained. Leaching of a 40 g portion of silicon was performed in a 400 mL thermostable beaker for duration of 1 h in a sand bath using a PE6110 magnetic stirrer (100 rpm) with automatic heating. During the experiment, the solution temperature spontaneously reached 60 °C. Acid solutions of varying concentrations, expressed as weight percentages, were employed, including (wt. %): H_2SO_4 10; HCl 10; HNO_3 10; HF 4. These specific values of solvent concentrations were chosen based on the prior research experiences of other scholars [5; 28 – 30]. The liquid to solid ratio was maintained at 5:1 and the required volume of the reagent was calculated taking into account the density of the acid of the set concentration [31].

Results of particle size analysis of powdered metallurgical silicon

Результаты гранулометрического анализа порошкообразного металлургического кремния

Size class, μm	Recovery, %	Total recovery, %	
		"on the plus"	"on the minus"
+150.0 ÷ 200.0	0.72	0.72	99.95
+100.0 ÷ 150.0	4.64	5.36	99.28
+45.0 ÷ 100.0	27.14	32.50	94.64
+25.0 ÷ 45.0	29.80	62.30	67.50
+12.0 ÷ 25.0	23.51	85.81	37.70
+6.0 ÷ 12.0	6.87	92.68	14.19
+3.0 ÷ 6.0	3.48	96.16	7.32
+1.5 ÷ 3.0	2.18	98.34	3.84
–1.5	1.66	100.00	1.66

Results and discussion

Following acid refining of silicon, the resulting solutions were analyzed for impurity content (Fig. 5) using atomic-emission analysis (AEA) through a PDA-8000 spectrometer (Shimadzu, Japan).

The best transfer of impurity elements to the solution was achieved when hydrofluoric acid was used as the solvent, resulting in concentrations of 2380 mg/dm^3 of iron,

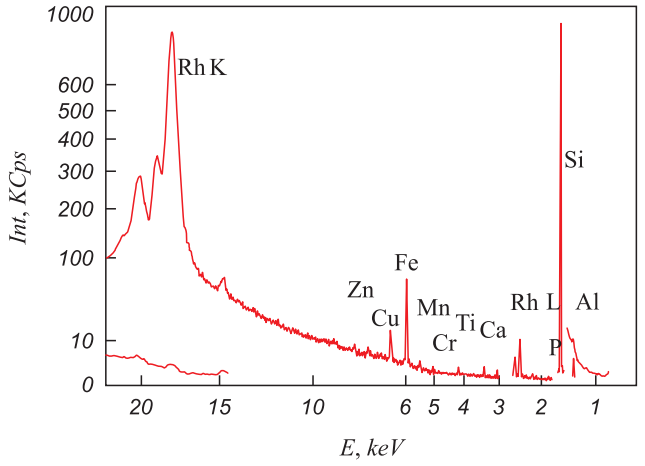

Fig. 4. *X*-ray spectrum of a sample of metallurgical silicon

Рис. 4. Спектр РФА образца металлургического кремния

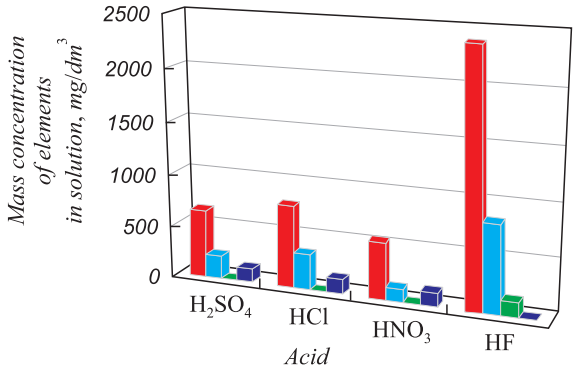

Fig. 5. Comparative histogram of impurities concentration in the solution of acid silicon refining:
– Fe; – Al; – Ti; – Ca

Рис. 5. Сравнительная гистограмма концентрации примесей в растворе кислотного рафинирования кремния:
– Fe; – Al; – Ti; – Ca

831 mg/dm^3 of aluminum, and 145 mg/dm^3 of titanium. The highest concentration of calcium transfer to the leaching solution was obtained using hydrochloric acid (with a concentration of 147 mg/dm^3).

These results demonstrate the potential use of the above acids for the deeper purification of metallurgical silicon obtained after oxidative refining at Silicon JSC. Experiments were conducted to leach impurities in the solution using acid mixtures. Ratios of sulfuric, hydrochloric, nitric, and hydrofluoric acids were selected as follows: 1:1, 3:1, and 1:1. The experimental conditions, including temperature, liquid-to-solid (L:S) ratio, stirring speed, and duration, remained unchanged. Fifteen experiments were conducted to leach impurities using various combinations of acid mixtures. The most effective results of impurity transfer to the solution of hydrometallurgical treatment of fine silicon are presented in Figure 6 (AEA data).

The mass concentration of titanium in the leaching solution was 2.77, 2.39 and 1.54 mg/dm^3, respectively, when using three acids in different ratios (H_2SO_4:HCl = 1:3, HNO_3:HCl = 3:1, HNO_3:H_2SO_4 = 1:3).

AEA results of the solutions after silicon hydrometallurgical refining showed that a mixture of sulfuric and hydrofluoric acids in a ratio of 1:1 was the most effective in transferring impurities to the solution. When this acid mixture was used as a solvent, the mass concentration of iron, aluminum, calcium, and titanium in the solution was the highest. The use of a mixture of sulfuric and hydrochloric acids as a solvent in a 1:3 ratio resulted in relatively high mass concentrations of impurity elements in the leaching solution (compared to the use of acids separately, except HF).

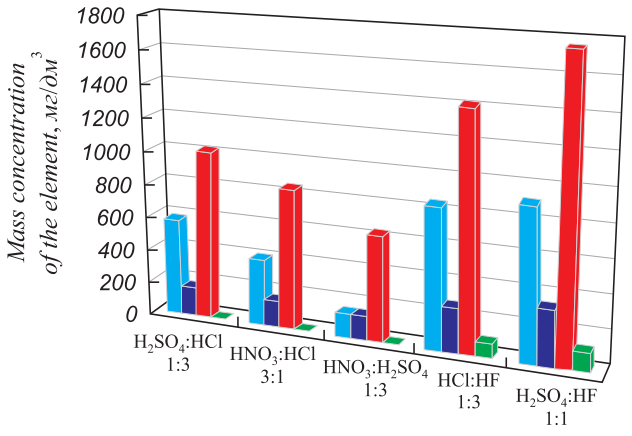

Fig. 6. Results of atomic emission analysis of silicon refining solutions:
– Al; – Ca; – Fe; – Ti

Рис. 6. Результаты атомно-эмиссионного анализа растворов рафинирования кремния:
– Al; – Ca; – Fe; – Ti

Conclusion

In this study, acid treatment was carried out on fine silicon samples to purify metallurgical silicon. Reagents such as 10 % solutions of hydrochloric, sulfuric, and nitric acids, as well as 4 % hydrofluoric acid, were used. These solvents were thermodynamically capable of interacting with impurity metal-containing compounds in silicon.

The use of hydrofluoric acid as a solvent resulted in the highest transfer of iron, aluminum, and titanium to the solution. Hydrochloric acid was found to be the most effective for calcium transfer. Furthermore, a mixture of H_2SO_4 and HCl at a ratio of 1:3 produced rather high mass concentrations of impurity elements in the leaching solution. The degree of iron removal was 33.32 %, aluminum – 54.64 %, calcium – 65.77 %, and titanium – 15.64 %. When a mixture of acids was used, a 1:1 ratio of sulfuric and hydrofluoric acids was found to be the most effective for maximum transfer of impurities to the solution, with the highest mass concentration of iron, aluminum, calcium, and titanium. The degree of removal for iron was 88.37 %, aluminum – 81.85 %, calcium – 94.62 % and titanium – 92.22 %. From an industrial standpoint, it is more economically and ecologically feasible to choose a mixture of 10 % sulfuric and hydrochloric acids at a 1:3 ratio for silicon purification.

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Information about the Authors / Сведения об авторах

Nina V. Nemchinova, *Dr. Sci. (Eng.), Prof., Head of the Chair "Non-Ferrous Metallurgy",* Irkutsk National Research Technical University
ORCID: 0000-0001-9895-1709
E-mail: ninavn@yandex.ru

Andrei A. Tyutrin, *Cand. Sci. (Eng.), Assist. Prof. of the Chair "Non-Ferrous Metallurgy",* Irkutsk National Research Technical University
ORCID: 0000-0001-9983-2680
E-mail: an.tu@inbox.ru

Anna A. Zaitseva, *Postgraduate, Assistant of the Chair "Non-Ferrous Metallurgy",* Irkutsk National Research Technical University
E-mail: vo1odkinaa@yandex.ru

Нина Владимировна Немчинова, *д.т.н., профессор, заведующий кафедрой металлургии цветных металлов,* Иркутский национальный исследовательский технический университет
ORCID: 0000-0001-9895-1709
E-mail: ninavn@yandex.ru

Андрей Александрович Тютрин, *к.т.н., доцент кафедры металлургии цветных металлов,* Иркутский национальный исследовательский технический университет
ORCID: 0000-0001-9983-2680
E-mail: an.tu@inbox.ru

Анна Александровна Зайцева, *аспирант, ассистент кафедры металлургии цветных металлов,* Иркутский национальный исследовательский технический университет
E-mail: vo1odkinaa@yandex.ru

Contribution of the Authors / Вклад авторов

N. V. Nemchinova – general scientific guidance, preparation of the manuscript.
A. A. Tyutrin – analysis of the obtained experimantal results.
A. A. Zaitseva – conducting of experiments, design of the graphic material.

Н. В. Немчинова – общее научное руководство и подготовка рукописи статьи.
А. А. Тютрин – анализ полученных результатов эксперимента.
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