Investigation of the behavior of gallium and indium in a metallurgical system characteristic of blast furnace hearth conditions

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In recent decades, there has been a growing interest in studying the behavior of trace impurity elements at all stages of ferrous metal production. This is driven by the processing of low-grade ores with complex chemical compositions and the use of secondary materials "enriched" with trace elements. Analysis of metallurgical raw materials and products reveals the presence of up to 40 elements from the periodic table in quantities exceeding 5 ppm. The rapid development of the electronics industry has driven growing interest in secondary resources of gallium and indium, which are critically important for semiconductor manufacturing. A metallurgical system was investigated, comprising pig iron, blast furnace slag, and lead as its main components under conditions characteristic of a blast furnace hearth. Gallium and indium were introduced into the system via various methods encapsulated in aluminum foil. In all experiments, an almost complete separation of gallium and indium between the pig iron and lead phases was achieved. Up to 99 % of the gallium introduced into the system partitioned into the pig iron, while 90–95 % of the introduced indium partitioned into the lead. The presence of small quantities of gallium and indium in the graphite phase suggests the potential for the formation of these metals' carbides under blast furnace conditions. A significant transfer of manganese sulfides into the lead-based phase was also observed in the investigated metallurgical system.
Key words: blast furnace, cast iron, trace elements, element flow, lead, carbides, sulphides, gallium, indium.
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Introduction

In recent decades, there has been a growing interest in studying the behavior of trace impurity elements at all stages of ferrous metal production. This is driven by the processing of low-grade ores with complex chemical compositions, which are "enriched" with trace impurities, as well as by the utilization of secondary materials, such as scrap metal, sludges, and slags, which are significantly contaminated with trace elements. Furthermore, blast furnace ironmaking has begun to utilize waste from other industries (primarily plastics and oil refining by-products), which contain trace impurities [1–6].

Concepts for the implementation of micro-blast furnace designs are being developed to process metallurgical secondary resources based on the briquetting of iron-bearing and fuel raw materials. Micro-blast furnaces are classified as units with a useful volume of up to 100 m^3 and a productivity of up to 300 tons per day. Such "small-scale" blast furnace ironmaking allows for the utilization of fine-grained iron-containing materials, coke breeze, charcoal, etc. The use of ore-coal briquettes minimizes the requirement for high-quality merchant coke with a high Coke Strength after Reaction (CSR) index to form the coke packing, which has a positive impact on operational efficiency [7–9].

Analysis of metallurgical raw materials and products has revealed the presence of up to 40 elements from the periodic table in quantities exceeding 5 ppm [10]. However, "*the blast furnace process represents a complex object of study, as the metallurgical system formed within the furnace encompasses all types of environments: gaseous, liquid, and solid, and is characterized by intricate patterns of mass transfer processes within a counter-current system across a wide range of temperatures and pressures*" [11]. To investigate the behavior of trace elements in the blast furnace smelting process, the concept of an "element flow" was introduced (analyzing the movement of an element throughout the entire production cycle, and subsequently, its "global life cycle") [12].

A similar methodology—MFA (Material Flow Analysis)—was adopted for application to metallurgical regions and, specifically, to the conditions of the blast furnace process around the turn of the century in EU countries. It was employed to describe the behavior of trace elements, particularly heavy metals [13–15].

The behavior of trace impurity elements in the blast furnace process was included as a dedicated section in the monograph by G.-W. Gudenau [16]. Detailed studies on the behavior of trace elements in blast furnace smelting have been conducted by GEO Partner AG (Switzerland), Baotou Iron and Steel (Group) Co., and the Christian Doppler Laboratory (Austria). Their findings have been consolidated in the doctoral thesis by Verena Trinkel [17].

A characteristic trace impurity found in virtually all raw materials of ferrous metallurgy is gallium. Research on the behavior of gallium in metallurgical processes has been conducted at NUST MISIS [18]. In contrast, the behavior of indium in the blast furnace process remains largely unexplored. It is known to be present in Mikhailovskoye Iron

Table 1. Contents of indium and lead in selected metallurgical materials from Blast Furnace No. 4 of PJSC Severstal after tapping [10]

Material	Content, ppm	
	Induim	Lead
Sow iron with slag inclusions	7	trace
Deposits on the charging device	30	1.600
Metal from the hearth lining	400	the major share

Ore Deposit. Indium has been detected in several metallurgical materials extracted from Blast Furnace No. 4 of PJSC Severstal (**Table 1**) [10].

The active development of the electronics industry, coupled with the fact that gallium and indium are widely used in semiconductor industry, is driving increased interest in these metals, including the utilization of their secondary resources.

Two-phase diagrams of the iron-lead-gallium and iron-lead-indium systems have been published [19]. The solubility of gallium in iron is high; under blast furnace smelting conditions, all gallium is expected to partition into the pig iron. Furthermore, it is known that the solubility of indium in lead is nearly 100 %. Consequently, indium can partition into lead, which forms a separate phase during the blast furnace process [16–17]. Gallium and lead melts undergo liquid-phase separation. It can be hypothesized that a near-complete separation of gallium and indium occurs between the pig iron and lead phases during blast furnace operation. However, this process may be influenced by the presence of active elements in the system, such as sulphur, carbon and silicon.

Thermodynamic modeling of gallium behavior in systems characteristic of the blast furnace process has shown that under reducing conditions at temperatures up to 700–800 °C, gallium is present in the system as an oxide [18]. As the temperature increases, active reduction of gallium and its dissolution in freshly reduced iron occur. At temperatures above 1500 °C, the sublimation of gallium from the liquid metal commences.

The most complex behavior is observed in systems containing sulphur. In this case, across all variants of redox conditions (ratios of carbon, hydrogen, and oxygen), a region of gallium sulfide stability is present within the temperature range of 600–1100 °C. Furthermore, the amount of gallium in the form of sulfide increases with a rising reducing potential of the system.

Thermodynamic modeling of indium behavior in systems characteristic of the blast furnace process has demonstrated that under conditions corresponding to the tuyere zone of a blast furnace, indium is expected to transition into the gas phase. The stability of indium oxide (In_2O_3) under blast furnace conditions lies within the temperature range of 300–500 °C; therefore, the transfer of indium into the slag is possible but unlikely. At temperatures above 500 °C and up to 1450–1650 °C, a region of stability emerges for indium dissolved in lead.

The aim of this work is the physical modeling of processes occurring in the blast furnace hearth with gallium- and indium-containing materials.

Methods of conducting the experiment

At NUST MISIS, three series of melting experiments were conducted. The charge of the first series (comprising 5 melts) consisted of pig iron, blast furnace slag, lead, gallium, indium, and aluminum foil used to encapsulate the low-melting-point metals. The approximate mass ratio of the components was as follows (in mass units): pig iron – 100, slag – 50, lead – 10, aluminum foil – 10, gallium and indium – 1 each (the total charge mass for each melt ranged from 200 to 240 g).

A foundry pig iron with high phosphorus content (mass fraction, %: Si – 1.55; Mn – 1.15; Cr – 0.27; Ni – 0.11; Ti – 0.08; S – 0.04; P – 0.125) and a blast furnace slag from ferromanganese production with high sulphur and manganese content (mass fraction, %: SiO_2 – 31.45; CaO – 40.88; Al_2O_3 – 9.80; MgO – 7.45; MnO – 8.12; S – 2.98) were used.

Blast furnace slag and pig iron were initially charged into graphite crucibles. The crucibles were placed in an AB UTENOS furnace (**Table 2**), followed by heating to approximately 1500 °C over 20 min under an air atmosphere to achieve complete melting and separation of the iron and slag. Subsequently, pre-weighed amounts of lead, indium, and gallium encapsulated in aluminum foil were introduced into the slag layer, and the melts were stirred. The duration of the melts ranged from 15 to 26 min, which allowed for obtaining samples with varying degrees of separation between the slag, pig iron, and lead phases.

The charge for the second series (comprising 5 melts) consisted of (mass units): 100 units of gallium-containing pig iron from the first series of melts, 50 units of slag, and a pre-prepared "master alloy" of lead, indium, and gallium in a 10:1:1 ratio.

Table 2. Main parameters of the TESCAN VEGA 3 scanning electron microscope

Parameter	Description	Value
SEM HV	Accelerating Voltage	20.0 kV
SEM MAG	Resolution	200x
WD	Distance from the emitter to the sample surface	15.49 mm
SM	Imaging mode	Resolution
DET	Image acquisition	BSE (Backscattered Electrons)

The charge for the third series (comprising 2 melts) included (mass units): 100 units of gallium-containing pig iron from the first series of melts, 50 units of slag, and 10 units of indium-containing lead from the melts of the initial series (where complete separation of metallic phases was achieved).

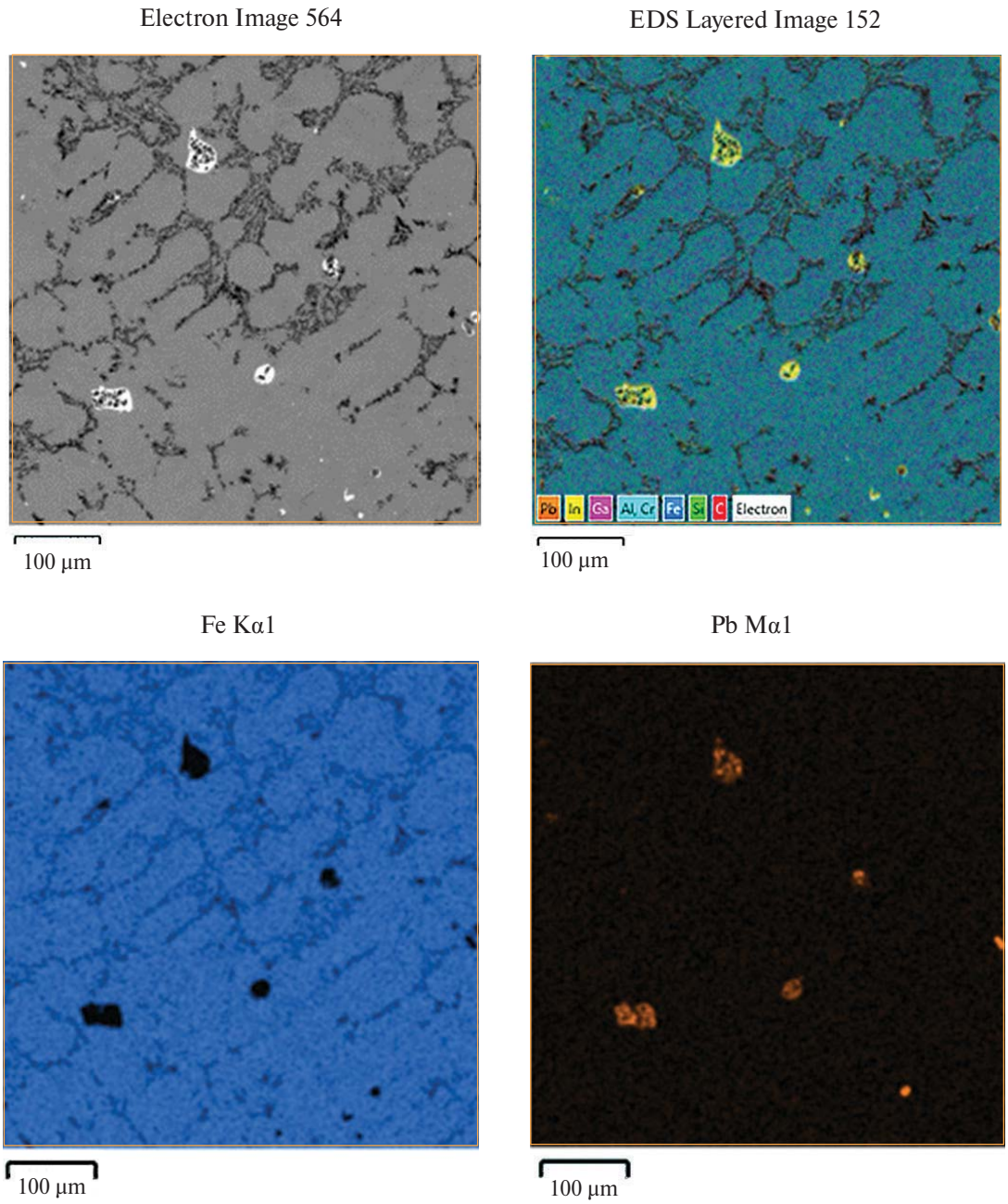
The experimental procedure for the second and third series was analogous to that of the first series melts. The "master alloy" and pre-crushed indium-containing lead were introduced into the slag melt wrapped in aluminum foil.

Results and Discussion

Samples of pig iron and lead, prepared using diamond cutting and grinding, were examined using a TESCAN VEGA 3 scanning electron microscope. In all experiments terminated prior to the complete separation of the pig iron and lead molten metal phases, a similar structure of the primary phase formation was observed (**Fig. 1**).

The studied samples are primarily composed of iron with dissolved gallium in the original component ratio (90–94 mass units of iron to 1 unit of gallium, D 1, S 5). Certain graphite inclusions contain indium and gallium, indicating the potential formation of indium and gallium carbides (**Fig. 2, Table 3**).

The lead inclusions contain remnants of aluminum foil, manganese sulfide (some manganese sulfide inclusions contain indium), and an indium-"enriched" phase (**Fig. 3, Table 4**). The manganese sulfide phase corresponds almost



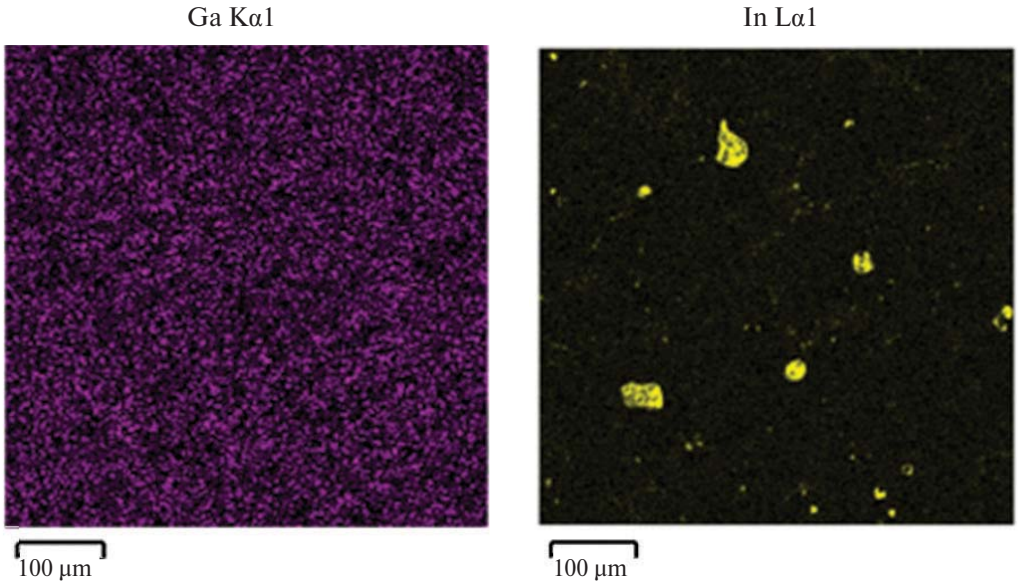


Fig. 1. Micrograph (500x magnification) of the upper section of a sample obtained after a 15-min holding time, exhibiting incomplete separation of the iron-based and lead-based phases (The grayscale image represents electron microscopy, while the color image corresponds to Energy Dispersive X-ray Spectroscopy (image scale: 100 μm, α1 – intensity line))

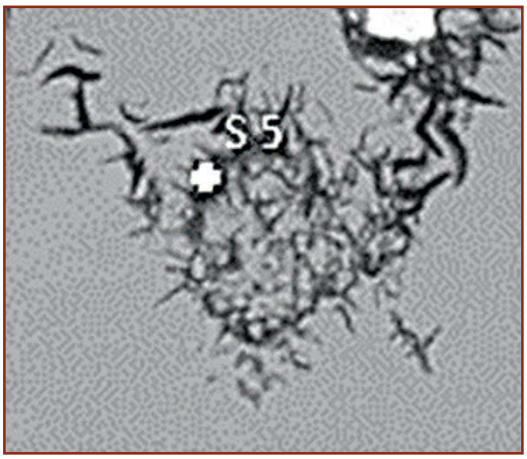


Fig. 2. Micrograph (2000× magnification) of the central section of a sample obtained after a 15-minute holding period, showing incomplete separation of the iron-based and lead-based phases, with graphite inclusions

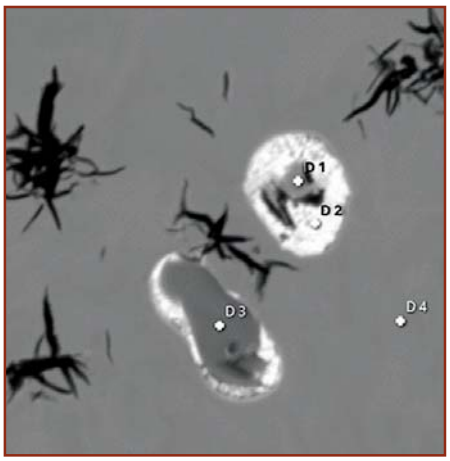


Fig. 3. Micrograph (2000× magnification) of the central section of a sample obtained after a 15-minute holding period, showing incomplete separation of the iron-based and lead-based phases, with manganese sulfide inclusion

Table 3. Content of primary phases at the analysis point (Fig. 2), mass fraction, %

Spectrum Label	C	Fe	Ga	In
S 1	56.82	39.92	0.46	1.21
S 2	23.83	70.4	0.63	1.78
S 3	47.79	49.46	0.44	0.4
S 4	49.05	48.5	0.51	–
S 5	4.38	90.33	0.96	–

Table 4. Content of primary phases at the analysis point (Fig. 3), mass fraction, %

Spectrum Label	S	Mn	Fe	Ga	In	Pb
D 1	–	0.58	93.4	0.89	2.2	–
D 2	–	–	2.98	–	87.71	8.62
D 3	37.59	60.86	1.55	–	–	–
D 4	–	0.55	95.1	1.31	–	–

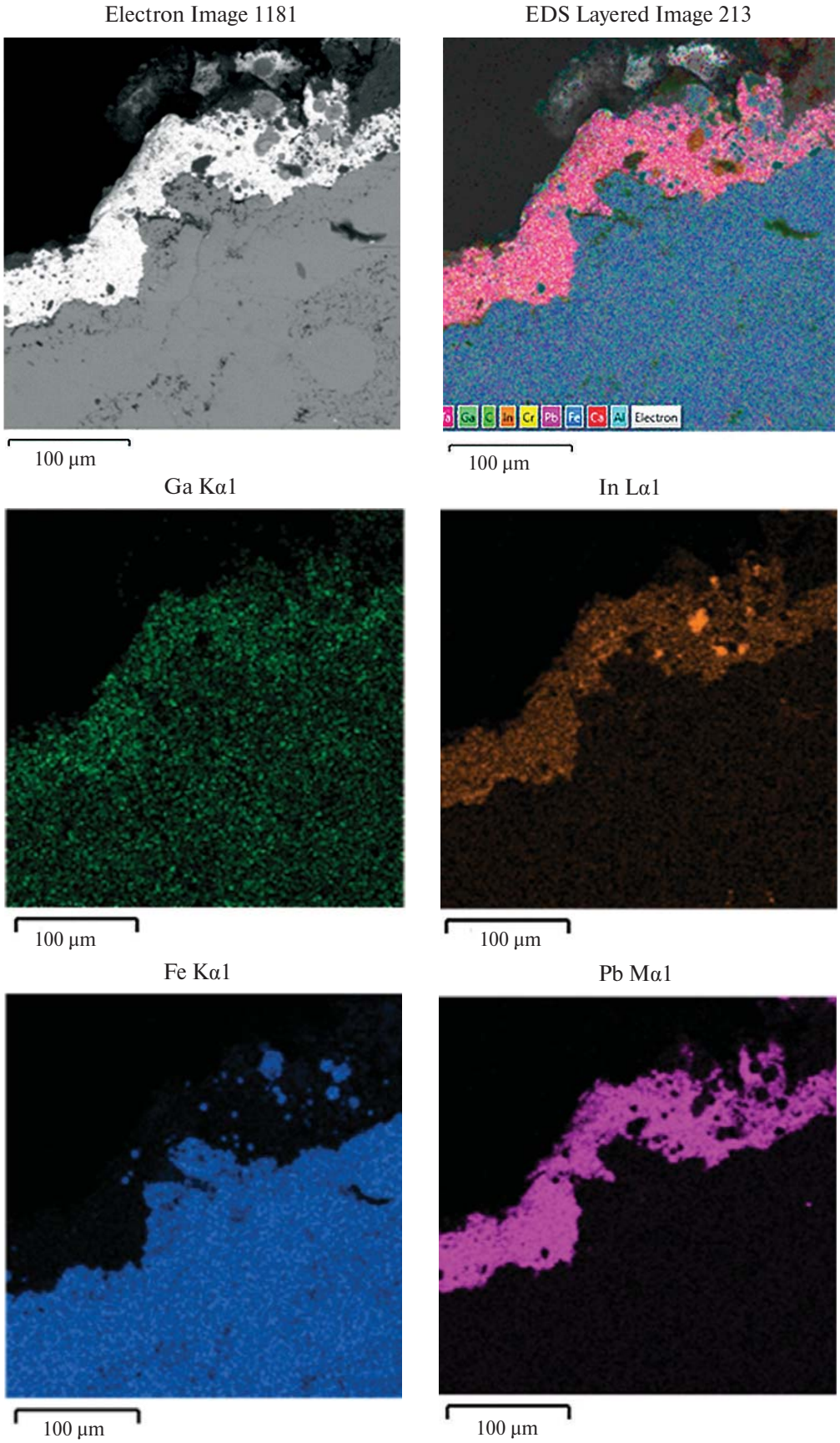


Fig. 4. Micrograph (500× magnification) of the central section of a sample obtained after a 15-minute holding period, showing incomplete separation of the iron-based and lead-based phases (the grayscale image represents scanning electron microscopy, while the color image corresponds to energy-dispersive X-ray spectroscopy (image scale: 100 µm, α1 – intensity line))

exactly to its chemical formula (D 3, with 33–35 units of sulphur per 54–58 units of manganese). When indium is present in this phase, its concentration ranges from 1.5 % to 3.5 %. The indium-enriched phase (D 2, within the "lead shell") has the following composition: approximately 80 % indium, about 20 % lead, with minor iron impurities (up to 1. 5%).

The lead-base phase, which is forming in the bottom part of an ingot (**Fig. 4**) excludes foil and slag remains, while indium is presented only in lead and galliun – only in cast iron.

Conclusions

1. In the metallurgical system comprising pig iron, blast furnace slag, and lead as its main components under conditions characteristic of a blast furnace hearth, an almost complete separation of gallium and indium between the pig iron and lead phases is achieved. Up to 99 % of the gallium introduced into the system partitions into the pig iron, while 90–95 % of the introduced indium partitions into the lead.

2. The presence of small quantities of gallium and indium in the graphite phase indicates the potential formation of these metals' carbides under blast furnace conditions.

3. A significant transfer of manganese sulfides into the lead-based phase is observed in the investigated metallurgical system.

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