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MODERN METHODS OF ANALYTICAL CONTROL OF INDUSTRIAL GASES

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Modern gas analysis requires an integrated approach to ensure the necessary metrological characteristics and achieve high reliability of detection. A new algorithm for multisensor systems based on synthesized domestic materials possessing semiconductor properties has been developed for the analysis of a wide range of gases of metallurgical industries. The use of gas-sensitive elements made of semiconductor material with *n*-type conductivity allows solving the main task of modern gas analysis – detection of vapors and gases of a wide range with high stability, necessary selectivity and sensitivity. Due to the developed surface structure formed from polycrystals 3-10 nm in size, semiconductor sensors allow to detect various substances in air in a wide range of concentrations: from trace amounts of 10^{-6}-10^{-5} mg/m^3 to high 500-800 mg/m^3. Increase of the selectivity of the sensors is facilitated by the introduction of catalysts into the gas-sensitive layer of doping impurities. The formation of multisensory systems increases degrees of freedom, expanding the range of identification of the analytes. In addition to solving the analytical task of forming gas sensitive elements, digital circuit and aerodynamic solutions have been developed that meet the requirements of gas analysis in a wide range of impurity concentrations and application conditions.

***Key words**:* semiconductors, chemisorption, industrial gases, analyte substances, gas sensitive sensors, information networks

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Introduction. Most of the technologies for obtaining ferrous, non-ferrous metals and alloys, carrying out various operations in the metallurgical and mining industry are associated with the implementation of heterophase processes and reactions (blast furnace, oxygen-converter, autogenous production, melting in vacuum furnaces, etc.), accompanied by the evolution of the gas phase.

The qualitative and quantitative composition of the gaseous medium, as one of the reaction phases, the dynamics of the change in the content of its individual components over time, have a great influence on the course of the technological process and on the quality of the final product

In many metallurgical processes there are stages with the release of combustible and explosive gases. Emissions of harmful and toxic industrial gases are the main component of environment pollution during the operation of metallurgical enterprises.

At the enterprises of non-ferrous and ferrous metallurgy a significant amount of waste gases is formed, they contain sulfurous anhydride, fluorine, chlorine, various inorganic and organic substances. Utilization and neutralization of these gases before their release into the atmosphere are of great importance both for solving the problem of complex use of raw materials and for protecting the air basin from pollution.

In non-ferrous metallurgy, the main gases released are:

– Sulphurous gas formed during the thermal treatment of sulfide ores in quantities exceeding the MPC;

– hydrofluoric, silicofluoride and fluoroorganic compounds, corresponding to processes of electrolysis and melting of cryolite in aluminum production;

– chlorine and hydrogen chloride during chlorination roasting and hydrochemical preparation of non-ferrous metals;

– arsenic and cyanide hydrogen, found in gold mining, tin, zinc and other non-ferrous metallurgy.

The list of process gases is quite extensive, and the diagnostics of the gas composition is analytically complex. In modern instruments, regardless of their technical complexity, a large set of sensors is required for the analysis of process gases, practically for each substance sampled.

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Traditional chemical methods [2, 7], used today, do not provide reliable analytical control of pollutants in accordance with modern requirements for chemical safety and environmental protection, while analytical systems composed of semiconductor sensors allow conducting analysis of a wide range of spectrum of gases in metallurgical industries without primary converters. They can analyze such as gases as SO_2, NO_2, HF silicofluoride and fluorocarbon gases, Cl_2, H_2, F_2, HCl, HCN, H_3As, CO, CO_2, H_2S, C_mH_n, combustible gases.

To improve the validity and reliability of gas analytical measurements that meet the modern requirements of analytical control, there have been developed semiconductor sensors [1, 3], used as primary converters, and unified gas analytical systems and devices of various types based of this technology: from miniature portable analyzers to gas analytical equipment in portative and stationary version [4, 5].

Based on semiconductor sensors, analytical systems have been created, designed to control the atmosphere at objects of almost any complexity [6]. The sensitive layers are made of tin and transition metal oxides: SnO_2, ZnO, NiO, Cu_2O, In_2O_3, etc., which are semiconductors with intrinsic conductivity of *p*- or *n*-type, enriched with antimony and doped with Pb, Pd, Ag, Co, Mn catalysts and a number of other elements [9].

Methods of research. The authors of this paper have developed budget semiconductor sensors in nanostructural form with the help of original synthesis techniques, topography of deposition and sintering of oxide films possessing semiconductor properties: SnO_2, TiO_2, WO_3, V_2O_5, In_2O_3, Fe_2O_3, Cu_2O, CuO, ZnO, CdO, etc. with the following properties: high sensitivity, selectivity, stability of operation, low mass-size dimensions and power consumption (Fig.1).

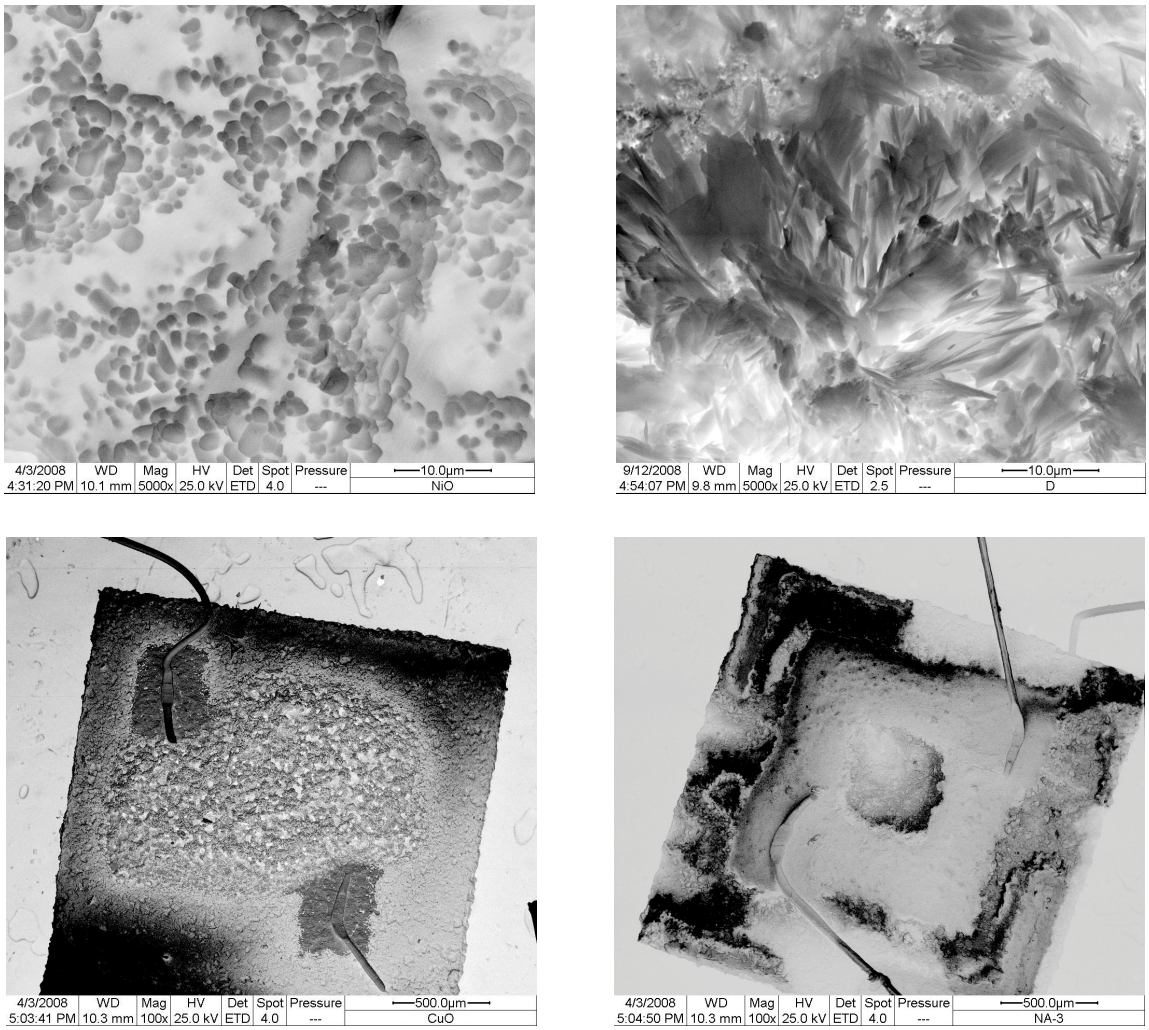


Fig.1. Raster image of the surface of semiconductor gas sensitive sensors based on SnO_2 doped with antimony oxide (III)

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On the dielectric substrate Al_2O_3, electrical contacts, a heating element and a sensitive layer are applied on each side by screen printing. Contact groups and a heating element are formed from conductive and resistive silver– and gold-containing pastes. The paste for applying the gas sensitive layer is made from synthesized oxides. After the application of the semiconductor layer, the paste is sintered on the substrate at a temperature of 850 °C. Each substrate is cut by the laser into separate elements, which are mounted in the working frame by means of thermal contact welding. The shells are designed for the installation of 1, 2 and 4-gas sensitive elements.

The developed structure of the surface of the created materials of the gas-sensitive layer is achieved by a specific synthesis procedure, heat treatment of the obtained xerogel and technological methods. The specific area of the working surface is 90-120 m^2/g. For example, semiconductor structures of *n*-SnO_2 enriched with Sb to provide activation barriers at heterointerfaces of polycrystals have been used to create resistive temperature sensors with temperature control of the forbidden band width.

The principle of operation of semiconductor sensors is based on measuring the change in the electrical conductivity of a gas sensitive layer upon adsorption of gaseous substance molecules on its surface. In an oxygen atmosphere, the value of the electrical conductivity of a gas sensor is stable and determined by the concentration of charge carriers (electrons) transferred from the valence band to the conduction band for a given thermal action. During adsorption of molecules of a gaseous substance on the surface of a gas sensitive layer, the equilibrium value of the current strength in the conduction band is violated and either an increase in the carrier concentration (during chemisorption of the donor gas) or a decrease in their concentration (during chemisorption of the acceptor gas). Changes in the number of charge carriers determine the analytical response of the sensor, which depends on the chemical composition of the analyte gas and its concentration.

Improvement of selectivity and sensitivity of the gas-adsorption layer is achieved by introducing metal catalysts into the composition of the semiconductor and controlled heating, which maintains the sensor surface temperature from 100 to 1000 °C by means of pulse width modulation (PWM), which allows setting the heating power values with high accuracy.

To increase the selectivity of detection and the possibility of spectral processing of measurement results, the authors proposed to use of a multichannel circuit composed of semiconductor sensors as a detector of gas analytical systems, the number of independent channels is a multiple of 2^n (4, 8, 16, etc.).

The algorithm for processing the obtained data is based on self-similar transformations that do not require the introduction of additional parameters for identification and concentration calculations. The applied mathematical apparatus ensures the stability of the indicator effect of the sensors during a long period of operation. The high manufacturability of created gas-sensitive microchips and the developed algorithm for processing information do not require a re-calibration of the analytical component of gas analyzers.

The developed gas analysis systems allow changing the range of detectable substances without replacing the sensor set with by connecting an external PC. The number of simultaneously analyzed gases is determined by the number of channels, the adsorption capacity of the gas phase substance, the chemical composition of the sensor, and the heating temperature.

The developed equipment and technology on the basis of semiconductor sensors and their systems have the following advantages: simplicity of operation; completeness and reliability of the results; autonomy, independence from power supplies, and automatic mode of operation.

According to the change of the electrical conductivity sine of a gas sensitive adsorption material, the main gaseous substances of various metallurgical industries are classified according to the following groups:

- SO_2, NO_2, H_2, H_2S – I group (Fig. 2, *a*);
- HF, Cl_2, F_2, HCl – II group (Fig. 2, *b*);
- silicofluoride and fluorine-organic gases, HCN, H_3As – III group;
- C_mH_n, flammable gases – IV group.

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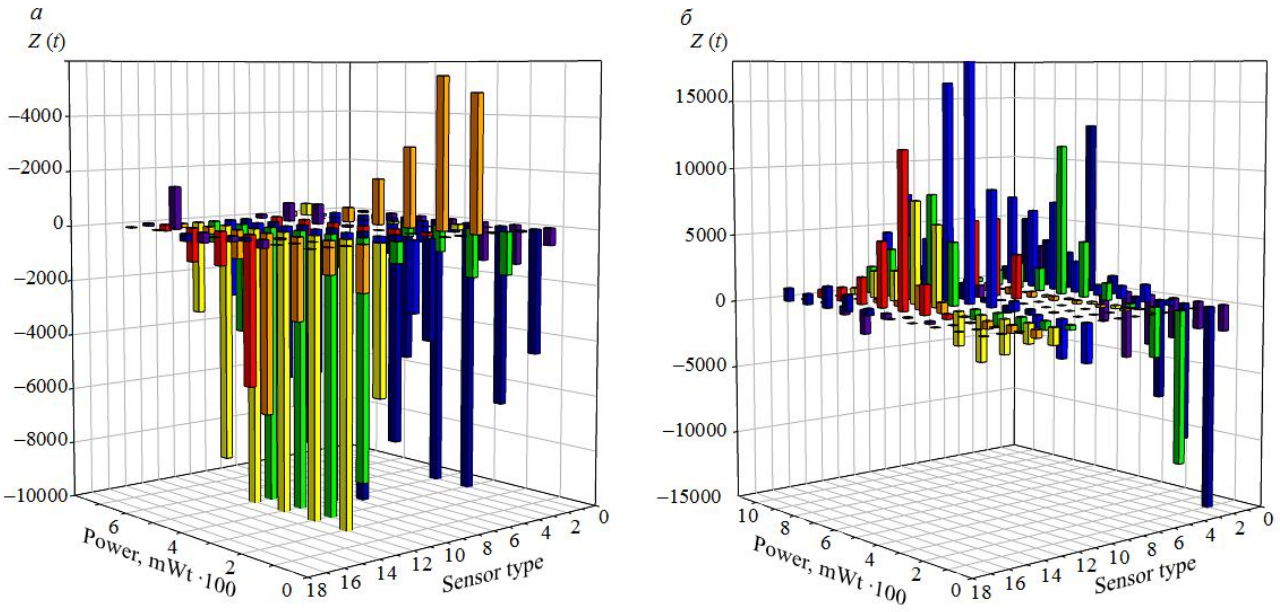


Fig.2. Examples of group detection of analyte substances ($Z(t)$ – an analytical signal proportional to the change in the electrical conductivity of the gas sensitive layer as a result of chemisorption of analyte)

a – analytical signals for group I; *b* – analytical signals for group II

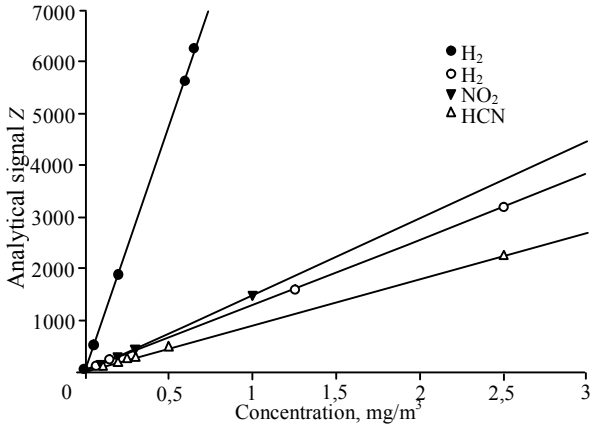


Fig.3. The dependence of the analytical signal, based on the measurement of the electrical conductivity of the gas-adsorption layer, on the concentration of analyte substances simultaneously present in the gas phase

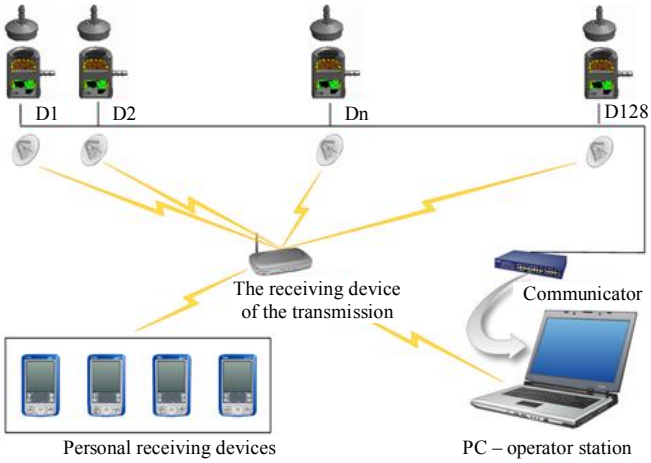


Fig.4. Scheme of connection of gas analyzers in the information network

These groups are formed by the operator and alternated automatically according to the application and detection algorithm. To increase the reliability of the identification of detectable substances, it is advisable to reduce the number of analytes in the group as the number of groups increases.

The concentration of the components to be determined is calculated from the coupling equations obtained from the calibration vapor-gas mixtures (Fig. 3).

Gas analyzers of stationary, portative and portable types have been developed, which can be mounted on various objects, including constructively complex ones. The miniature size of the developed devices does not require any special work for their installation.

The devices like gas analytical systems, can be integrated into existing local networks and warning systems (Fig.4). The design solutions provide the introduction of wireless communication with both the operator and the centralized control room of the facility.

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An important part of gas analytical systems and devices built on the basis of semiconductor sensors is a system of sampling and sample preparation, the its hardware design depends on the specific task of the analysis.

The prospects and expediency of using the developed gas analytical systems in metallurgy are provided by high technical, analytical and metrological characteristics of the developed instrument.

With the help of gas analyzers and instruments based on the use of the adsorption-kinetic method of measurements with the use of semiconductor gas sensitive sensors, it is possible to solve various control problems [6]:

• gas phase and fuel combustion efficiency at thermal power plants;

• composition of natural gas during its extraction, transportation, liquefaction and other types of processing;

• microimpurities in the production of technical oxygen, nitrogen and argon;

• atmospheric emissions of nuclear power plants.

Portative and portable types of gas analyzers can be used for geological exploration and environmental monitoring.

Conclusions

1. There has been developed the technological scheme for the production of semiconductor gas sensitive materials with selective properties with respect to a wide range of gases from metallurgical industries such as SO_2, NO_2, HF, silicofluoride and fluorocarbon gases, Cl_2, H_2, F_2, HCl, HCN, H_3As, CO, CO_2, H_2S, C_mH_n.

2. Control of the selectivity and sensitivity of the adsorption layer to a wide range of gaseous substances is achieved by introducing into the composition of the semiconductor metal catalysts and controlled heating catalysts, which enable maintainance of the surface temperature of the sensor in the range from 100 to 1000 °C with high accuracy.

3. The formation of multisensory systems based on the uniformity of the variation in the electrical conductivity of a gas sensitive adsorption material allows us to isolate groups of analyte substances which content can be determined simultaneously without changing the type of the adsorption layer of the semiconductor.

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