CHEMISTRY

Academician of the Academy of Sciences of the BSSR M. M. PAVLYUCHENKO, K. V. DUBOVIK

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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DEPENDENCE OF THE INTENSITY OF SPECTRAL LINES OF TRACE ELEMENTS IN A SILICATE SYSTEM ON ITS PHASE DIAGRAM

The study of the mechanism by which "third elements" exert their influence requires knowledge of the processes by which components pass from the matrix into the discharge plasma. In works (1-3), the anomalous entry of elements, considered for the main components of binary metallic systems, was compared with liquid–vapor phase diagrams. In the present work, the regularity in the change of the entry of trace elements with changes in the composition of a silicate base was studied as a function of the solid phase–liquid phase diagram. The objects of investigation were binary silicate systems: SiO_2–Al_2O_3, SiO_2–MgO, Al_2O_3–MgO. The concentration of each oxide in the system was varied from 0 to 100%. Solutions of salts of copper, silver, cobalt, and nickel were introduced into all standards of the system in equal amounts (0.1% of the element). The samples were evaporated from the crater of a carbon electrode in an alternating-current arc with a current of 16 A. The spectra were recorded on a DFS-3 spectrograph.

Fig. 1. Dependence of the intensity of the lines of trace elements: copper (a), silver (b), cobalt (v), nickel (g), and of the silicon line (d) on the composition of standards of the SiO_2–Al_2O_3 system; 1–before sintering, 2–after sintering (curves 2 and d are shifted along the ordinate axis)

Under a stable regime of the light source, a monotonic change in the concentrations of macrocomponents from one standard to another in one system does not, as has been shown experimentally, cause sharp changes in the temperature and excitation conditions in the arc plasma. Under these conditions, the complex dependence of the function $I = f[C]$ for the lines of trace elements in the silicate systems considered is caused by the entry of the substance of the standards into the gas cloud. This dependence for all trace elements in each system is qualitatively of the same character and is in agreement with its phase

Figure 2

Figure 2: Figure 2

diagram. At the same time, the curves of the dependence of the intensity of the lines of impurity elements on the composition of the standards may either follow the diagram directly (the Al_2O_3–MgO system), or give its inverted image (the SiO_2–Al_2O_3 and SiO_2–MgO systems). The character of the relationship between the line intensity and the phase diagram of the system is determined by the peculiarities of evaporation of its components.

Analysis of the phase diagram of the SiO_2–Al_2O_3 system (Fig. 1) indicates that, upon cooling of the melt of standards containing from 5 to 72% Al_2O_3, along curve AB mullite passes into the solid phase and the liquid is enriched in ...

...with silica oxide [silicon dioxide] ([4]). In the crater of the carbon electrode a process occurs that is the reverse of crystallization. When the electrode reaches a temperature of 1545°C (the temperature of eutectic point B), the mixture of oxides in the indicated concentration range begins to melt. In this case the first portion of the liquid phase corresponds to the composition of the eutectic and contains predominantly silica. In this liquid, during melting, mullite crystals dissolve.

The melting sequence considered determines the presence, in the liquid phase of the standards of this concentration region, of silica not bound in a compound, the amount of which decreases as the content of Al_2O_3 in the standards increases. In this part of the diagram, the line intensities of the trace elements (curves 1) and of silicon (curve 3) change in the same way. On the dependence curve of the intensity of the silicon line on its content in the standards (curve 3), at low SiO_2 concentrations the formation of a small horizontal segment is noted. In the liquid phase of the standards corresponding to this segment, silica does not exist in free form, and its passage into the gas cloud is possible only in the form of a compound. For these same standards, anomalous entry into the discharge gap is also observed for alumina. In the region of the diagram from the pure component Al_2O_3 to eutectic point C, the directions of the curves of the dependence $S = f(C)$ for the lines of the impurity elements and of aluminum coincide. The presence of a minimum on curves 1, whose position coincides with the composition of mullite, may be connected either with the absence, in the liquid phase of a standard of the composition of point A, of components SiO_2 and Al_2O_3 not bound in a compound, with which impurity elements enter the gas cloud, or with the great strength of the bonds in mullite. The formation of an intensity minimum on the curves $I = f(C)$ for the lines of the principal components of binary metallic systems was noted in work ([5]).

Fig. 2. Dependence of the line intensity of trace elements on the composition of standards of the MgO–Al_2O_3 system. The designations are the same as in

Fig. 1.

The features of crystallization (melting) in the SiO_2–MgO system are in agreement with the obtained regularity in the change of trace-element line intensity with the composition of the standards. Preliminary sintering of standards of the SiO_2–Al_2O_3 and SiO_2–MgO systems, carried out in a muffle furnace at a temperature of 1500°C, practically eliminates, over a wide concentration interval, the influence of composition on the line intensity of impurity elements (Figs. 1, 2).

A distinctive feature of the Al_2O_3–MgO system (Fig. 2) is its ability to form solid solutions (mixed crystals). Upon complete melting of the mixed crystals in the crater of the carbon electrode, all elements of the standards simultaneously pass into the liquid phase. In this case the composition of the melt of each standard of the system corresponds to the composition of the mixed crystals formed in them. The simultaneous entry of all components into the gas cloud determines the coincidence of the maxima on the intensity curves and on the phase diagram (curves 1). Preliminary sintering of standards of the Al_2O_3–MgO system does not eliminate the influence of composition on the line intensity of trace elements and does not change the direction of this dependence (curves 2).

The observed relationship between the intensity of the lines of elements and the physicochemical state of the system reveals general regularities in the entry of the sample from the electrode crater into the discharge gap; knowledge of these regularities makes it possible to solve a number of practical problems in spectral analysis. At the same time, determining the nature of the dependence of the intensity of spectral lines on the composition of the matrix makes it possible to draw conclusions about the processes occurring in systems at high temperatures. Thus, the spectral method may prove useful for the physicochemical analysis of complex systems.

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