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Academician VIKT. I. SPITSYN, L. I. ZEMLYANOVA, I. E. MIKHAILENKO,

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Abstract

Full Text

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Academician VIKT. I. SPITSYN, L. I. ZEMLYANOVA, I. E. MIKHAILENKO, V. V. GROMOV, and I. E. ZIMAKOV

ELECTRON-MICROSCOPIC INVESTIGATION OF THE EFFECT OF RADIOACTIVE RADIATION FROM SOLIDS ON THE STRUCTURE OF THEIR SURFACE

It was shown earlier ([1]) that the radioactive radiation of solids substantially affects their physicochemical properties—their sorption capacity ([2–4]), solubility in water ([5–7]), and also influences the kinetics of heterogeneous processes of isotope exchange ([8–10]) and catalysis ([11–12]). One of the causes of these phenomena may be disturbances of the crystal lattice arising from the ionizing action of the emitted radiation and the appearance of recoil atoms, and, associated with this, changes in the surface structure of solids.

In the present work, the structure of the surface of radioactive samples of certain sulfates (potassium, magnesium, and barium), as well as molybdenum anhydride, with which investigations in the field of adsorption, catalysis, and isotope exchange had been carried out, was studied under an electron microscope. Electron-microscopic images were obtained by the replica method. Preparations of K_2SO_4, $MgSO_4$, and MoO_3 in the form of a fine powder were applied to a collodion film; then a layer of quartz 200-300 Å thick was vacuum-deposited onto the powder layer. After dissolving the collodion film in amyl acetate, the quartz replicas obtained were washed with distilled water in the case of K_2SO_4 and $MgSO_4$, or with a dilute alkali solution in the case of molybdenum anhydride, in order to remove particles of the substances under study that might have adhered to the replica. The films were then examined in an electron microscope. For $BaSO_4$ preparations, because of the poor solubility of the salt, the double-replica method was used, for which silver-quartz replicas were prepared.

Radioactive preparations of potassium and magnesium sulfates were obtained by introducing into them small additions of sodium sulfate containing S^{35} ([6]). $BaSO_4$ precipitates were isolated according to the previously described procedure ([2]). Samples of radioactive MoO_3 were prepared by mixing ordinary molybdenum anhydride with a preparation containing Mo^{99}, in a definite ratio to obtain the required specific radioactivity. The mixture was then converted by the action of an aqueous ammonia solution into ammonium molybdate, which was subsequently decomposed on heating. The MoO_3 obtained was sublimed at 850°. Data on the preparations studied are given in Table 1.

Figure 1 presents microphotographs of radioactive and nonradioactive preparations of K_2SO_4, $MgSO_4$, $BaSO_4$, and MoO_3, taken with an electron microscope at a magnification of 12,000 times.

On examining the images obtained, it may be noted that the surface of the crystals in the nonradioactive preparations is relatively smooth. The surface of the radioactive crystals proves to be highly developed. The introduction of a small amount of radium into the $BaSO_4$ preparation (Fig. 1, 3c) leads to a particularly sharp change in the structure of the surface of the crystals.

Table 1

Specimens studied

Specimen	Sample No.	Na_2SO_4 content, %	Specific activity of specimens, mCi/g at the moment of preparation	Specific activity of specimens, mCi/g during the experiment
K_2SO_4	1 a	–	0	0
K_2SO_4	1 b	3	19.0	19.0
K_2SO_4	1 c	3	98.8	0.3
K_2SO_4	1 d	–	0	0
K_2SO_4	1 e	3	10.8	10.8
$MgSO_4$	2 a	2.07	4.5	$1.7 \cdot 10^{-2}$
$MgSO_4$	2 b	21.87	180.6	$4.5 \cdot 10^{-2}$
$BaSO_4$	3 a		0	0
$BaSO_4$	3 b		5	0.03
$BaSO_4$	3 c		100	3.4
$Ba(Ra)SO_4$	3 d		$3 \cdot 10^{-7}$ in Ra	$3 \cdot 10^{-7}$ in Ra
MoO_3	4 a		0	0
MoO_3	4 b		4	3.9
MoO_3	4 c		8	7.7
MoO_3	4 d		14	13.5

Specimens of K_2SO_4, $BaSO_4$, and MoO_3 that were subjected to external irradiation by electrons with an energy of 800 keV also undergo certain changes in surface structure. It should be noted, however, that although the dose received by the specimens under external irradiation was considerably higher than in the case of radioactive radiation, the changes in the surface of the irradiated specimens prove to be less pronounced, as is evident, for example, from Fig. 1, *1e*. Similar microphotographs for the other irradiated specimens are not presented, since they differ only slightly from the corresponding nonradioactive specimens.

Table 2

Figure 1. Microphotographs of specimens: 1 –K_2SO_4, 2 –$MgSO_4$, 3 –$BaSO_4$, 4 –MoO_3. (For the designations of the specimens, see Table 1.)

Figure 1: Figure 1. Microphotographs of specimens: 1 –K_2SO_4, 2 –$MgSO_4$, 3 –$BaSO_4$, 4 –MoO_3. (For the designations of the specimens, see Table 1.)

Sieve analysis of radioactive and nonradioactive potassium sulfate samples

Hole size of the sieves, mm	Fraction content, % – nonradioactive specimen	Fraction content, % – radioactive specimen (10.8 mCi/g S^{35})
+0.28	2.51	0.01
−0.28+0.16	53.96	0.36
−0.16+0.13	15.94	1.29
−0.13+0.10	16.61	23.80
−0.10+0.09	2.41	16.84
−0.09	6.98	56.06

The observed surface disturbances occur almost uniformly throughout the entire crystal of the radioactive substance: no deep pits are observed, as is the case in specimens irradiated with neutrons ([13]). The changes in the surface of radioactive specimens outwardly resemble the phenomena that occur after etching metals by means of an ion beam ([14], [15]).

A comparison of Fig. 1, *1a* and *1b*; *4a* and *4b*, *4c*, *4d* makes it possible to conclude that disturbances of the surface of radioactive specimens occur already in the process of separation of the solid phase from a solution or gaseous medium. These disturbances develop and intensify as radioactive decay proceeds in the specimens studied (Fig. 1, *1b*). Apparently, the radiation of electrons, or of other charged particles, causes in the process of crystallization of solids the formation of many new active centers—nuclei of crystallization. Indeed, during the separation of radioac–

Fig. 1. Microphotographs of specimens: **1** –K_2SO_4, **2** –$MgSO_4$, **3** –$BaSO_4$, **4** –MoO_3.
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active salts from solutions, a change is observed in the particle-size distribution compared with nonradioactive preparations. The content of fine fractions increases considerably. As an example, Table 2 gives the results of sieve analysis of radioactive and nonradioactive preparations of K_2SO_4 crystallized under identical conditions.

As for the causes of the appearance of inhomogeneities on the surface of radioactive preparations, one may suggest that additional crystallization centers are created under the influence of radiation directly on the surface of radioactive salts, leading to the disintegration of larger crystals and, accordingly, to loosening of the surface (Figs. 1, 1d), and in some cases to the formation of a dendritic structure. The latter, for example, occurs during the release of molybdenum anhydride from the gas phase (Figs. 1, 4v and 4g).

The further development of the surface of solids under the influence of prolonged radioactive radiation is more reminiscent of the phenomenon of radiation corrosion ([14],[15]) than of the radiation growth of crystals discovered under neutron irradiation ([16]).

One of the sharp manifestations of the structural features of the surface of radioactive samples is revealed in adsorption processes ([2]-[4]). Thus, in the absorption of methanol, benzene, and hexane vapors by $BaSO_4$ precipitates, it was established that the adsorption of these gases per unit surface area in radioactive samples is considerably higher than in nonradioactive ones. This fact indicates substantial differences in the surface structure of radioactive and nonradioactive samples.

Institute of Physical Chemistry
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.