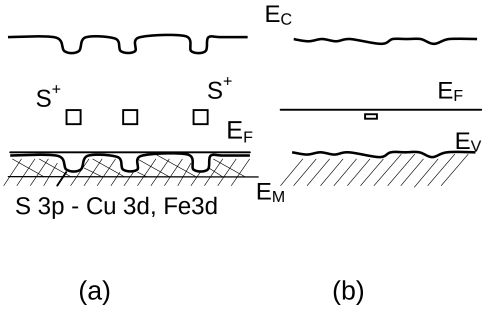
Passivation of Sulfide Minerals: Are the Metal-Deficient Layers Responsible?

Yu. Mikhlin, Ye. Tomashevich, A. Kuklinskiy, D. Shipin,
I. Asanov,[1] A. Okotrub,[1] V. Varnek,[1] N. Bausk[1]
Institute of Chemistry and Chemical Technology of SB
RAS, ul. K.Marksa, 42, Krasnoyarsk, 660049, Russia,
e-mail yumikh@icct.ru
[1]Institute of Inorganic Chemistry of SB RAS,
pr. Lavrent'eva, 3, Novosibirsk, 630090, Russia

Passivation is one of the most pressing problems of leaching and electrochemistry of sulfide minerals. The idea that the formation of elemental sulfur on mineral surfaces causes the passivation seems to be prevalent, although insoluble metal salts and oxyhydroxides are considered as candidates for this role as well. An alternative concept suggests that the metal depleted layers of metal sulfides formed due to preferential release of metal are responsible for the passivity as they conceivably retard electron or ion transportation towards the interface [1-3]. The presence of such layers was actually proved by XPS (see, for example, [2-4] and references herein), but it is still unclear which properties of the layers could make them passive. The passivation is usually eliminated at higher potentials, implying oxidation of elemental sulfur or decomposition of the metal-deficient layers.

We have studied the reacted surface layers of pyrrhotite, chalcopyrite, galena, arsenopyrite using XPS, X-ray spectroscopy and other techniques. The non-stoichiometric, metal-deficient layers at the sulfide minerals have been found to arise at various potentials in the course of the electrochemical polarization and as a result of oxidative leaching in ferric-bearing solutions. At potentials higher than ~0.7 V (vs. Ag/AgCl), in so-called "transpassive" region, the depletion of pyrrhotite, chalcopyrite, arsenopyrite in metals becomes particularly large, suggesting that the layers neither decompose nor are passive, in contrast with the conventional views. Moreover, pyrrhotite and chalcopyrite electrodes with thick, 1 μm or more, metal-deficient layers produced by the preliminary etching exhibit only minor differences in the electrochemical behaviour under the anodic biases. The examination of the layer structures shows no sign that the forbidden gap is increased relative to the intrinsic materials. These mean that in general the metal-deficient layers are not passiving agents. At the same time, an enhanced content of Fe^{3+}-O species has been detected on the passive surfaces of pyrrhotite; although it is unclear whether this phenomenon is a reason or a consequence of passivation [5].

However, there are a number of facts indicating that passivation is related with some special properties of the reacted surface layers. In particular, a correlation between the formation of high amount of donor-type defect centers D^+ and the passivation has been found. Then, the passivity can be related with rather strict atomic structures, which have either comparably low deficiency of a metal or high content of incorporated oxygen. The altered zones of metal sulfides is strongly disordered or/and amorphous, whereas it is well-known that the conductivity of the disordered semiconductors is often lower by several orders of magnitude than that of their crystalline counterparts [6-7]. Impurities affect the conductivity and other properties of conventional chalcogenide glasses only if they are located in fairly rigid environment [7]. On this basis, the mechanism for metal sulfide passivation has been developed, which uses the above and some other concepts of the physics of disordered semiconductors. The passivation is believed to be due to a substantial density of D^+-type centers stochastically distributed in the oxidized surface stratum of the reacted layer or in near-stoichiometric defective sulfide layer. The centers are related with positively charged sulfur atoms and, perhaps, with Fe^{3+} species in pyrrhotite and pyrite, Cu^{2+} in chalcopyrite and copper sulfides; spectroscopic data provide some evidences for such centers. These species are expected to cause large fluctuations of the potential in the solid (Fig. 1), Anderson localization of electronic states in the upper portion of the valence band, sharp decrease in the carrier mobility and the conductivity of the surface layer. It is possible that this effect entails a sequence of other events resulting in stronger passivity, for example, due to a formation of the ferric oxyhydroxide film.



(a) (b)

Figure 1. Electronic band structure diagram of the non-stoichiometric layer of chalcopyrite (a) under oxidation in the "passive" potential region, (b) during negative-going scan.

Acknowledgement

This research was supported by the Russian Foundation for Basic Research, Project 01-03-32687a.

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