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P. BALAŽ*, Z. BASTL** and V. VIGDERGAUZ***

INVESTIGATION OF THE SURFACE PHENOMENA IN MECHANICALLY ACTIVATED TETRAHEDRITE BY CYCLIC VOLTAMMETRY AND X-RAY PHOTOELECTRON SPECTROSCOPY

The properties of mineral tetrahedrite $Cu_{12}Sb_4S_{13}$ after mechanical activation in air were studied by the methods of cyclic voltammetry and X-ray photoelectron spectroscopy. The mechanical activation leads to generation of paramagnetic Cu^{2+} ions in comparison with non-activated tetrahedrite where in the surface only Cu^{1+} ions were detected. During activation enrichment of tetrahedrite surface with antimony was observed.

INTRODUCTION

The mechanical activation by intensive grinding is one of the methods that enable intentional generation of defects in solids and thus provide a control over their reactivity in subsequent processes, e.g., in leaching (Avvakumov 1986; Boldyrev 1987; Tkáčova 1989). Complex changes influencing the surface and bulk properties take place in the course of mechanical activation of sulphides.

The methods of X-ray photoelectron spectroscopy and cyclic voltammetry are frequently used for studying the surface composition and activity of sulphide minerals [Brion 1980; Buckley and Woods 1984; Buckley and Walker 1988–89; Buckley et al. 1989). X-ray photoelectron spectroscopy is sensitive to chemical environment of atoms and for this reason it is particularly appropriate for investigating the mechanically disordered surface of sulphides in which different oxidation products are formed by the effect of intensive grinding in air (Balaž and Ebert 1991; Balaž et al. 1991; Balaž et al. 1992). On the other hand, the application of cyclic voltammetry enables us to obtain information about the leaching behaviour of sulphides in following hydrometallurgical processes.

*Institute of Geotechnics of the Slovak Academy of Sciences, 043 53 Kosice, Slovakia.
**J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague, Czech Republic.
***Institute for Comprehensive Development of Mineral Resources of the Russian Academy of Sciences, 111 020 Moscow, Russia.

The aim of this work was to study the surface phenomena which take place during mechanical activation of tetrahedrite ($Cu_{12}Sb_4S_{13}$) in order to find changes in distribution of copper and antimony in surface layers of the mineral.

EXPERIMENTAL

Material. The investigations were carried out with the mineral tetrahedrite of general formula $Cu_{12}Sb_4S_{13}$ (Rudeany deposit, Slovakia) with the following composition: 33.40% Cu, 4.42% Fe, 30.74% S, 2.10% As, 5.02% Hg, 0.80% Zn, 20.24% Sb, 2.83% SiO_2, 0.43% insoluble rest. X-ray diffraction examination showed that the sample contained small amounts of pyrite and quartz besides tetrahedrite.

Mechanical activation. It was performed by intensive grinding in a planetary mill Pulverisette 4 (Fritsch, Germany) under the conditions: loading of the mill – 25 balls of 10 mm in diameter and 5 balls of 25 mm in diameter, relative acceleration – b/g=10.3, material of grinding balls and vial – tungsten carbide, dry grinding (air) 0–30 min.

Physico-chemical characteristics. The specific surface area (S_G) was calculated statistically from the particle distribution data measured on a sedimentation balance (Sartorius, Germany).

The cyclic voltammograms were recorded in three-electrode system. Besides the working mineral electrode, the auxiliary Pt-electrode as well as a reference AgCl-electrode were used. The working disc electrode was made of pyrographite (diameter of 3 mm) on which powdered tetrahedrite was deposited by means of a binder. The 3% suspension of fluoroplast in water was used as a binder. The conditions of measurements were: working solution – 0.1 N H_2SO_4 (pH 1.3), atmosphere – He, temperature – 25 °C, scan rate – 20 mVs^{-1}. The measurements were carried out on a potentiostat PI-50 equipped with a programmer PR-8 (Izmerite, Gomel, Ukraine), the current sensitivity being 1 $\mu A\ cm^2$. An X-Y recorder was used for recording of cyclic voltammograms.

The X-ray photoelectron spectroscopic measurements were performed on an instrument ESCA 3 MKII (VG Scientific, Great Britain) in 10^{-6} Pa vacuum. The electrons were excited by the AlK emission (h = 1486.6 eV). The transmission energy of electron analyzer was 20 eV and the width of entrance slit of the analyzer was 4 mm.

RESULTS AND DISCUSSION

The investigations of the surface changes in mechanically activated tetrahedrite are illustrated by cyclic voltammograms in Fig. 1 and by X-ray photoelectron spectra in Figs. 2 and 3.

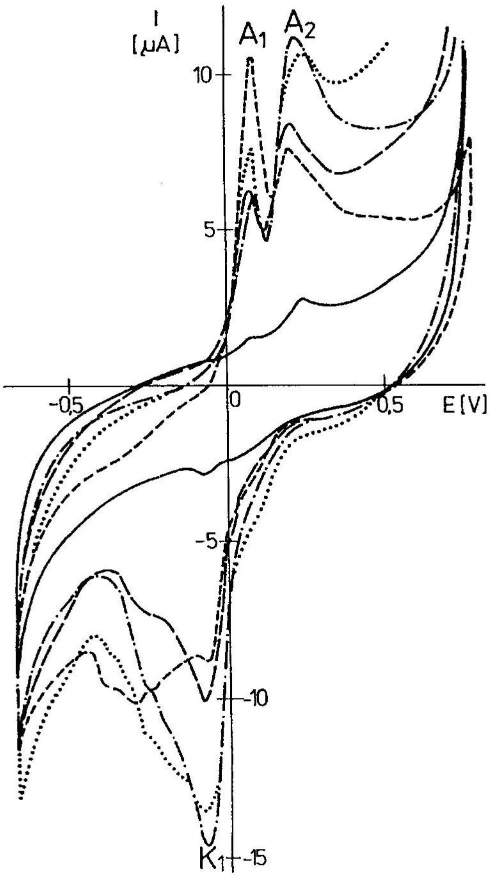

Fig. 1. Cyclic voltammograms of $Cu_{12}Sb_4S_{13}$, the third scan. Time of mechanical activation: (.......) 0 min, (——) 10 min, (....) 15 min, (–·–·–) 20 min, (– –) 30 min

The cyclic voltammograms are shaped by the sum of effects in anodic (A1, A2) and cathodic (K1) region. These effects are much more significant in the case of mechanically activated samples. The magnitude of anodic effect A1 increases up to the time of mechanical activation equal to 10 min (t_G = 10 min). At this time the specific surface area S_G reaches the maximum value of 0.28 m^2g^{-1}). The corresponding value of voltage E for the sample activated for 10 minutes is near to the thermodynamic potential of copper oxidation to the Cu^{+2} form. At higher times of mechanical activation effect A1 decreases in coherence with specific surface area decrease as a consequence of generation of agglomerates (Balaž et al. 1994). Simultaneously, both anodic effect A2 as well as coupled cathodic effect K1 increase. The position of effect A2 corresponds to antimony which we have registered on the cyclic voltammogram of antimonite Sb_2S_3 at equal potential under equal experimental conditions. We assume that the electrochemical activity of copper is screened by greater activity of antimony at higher values of potential. These data

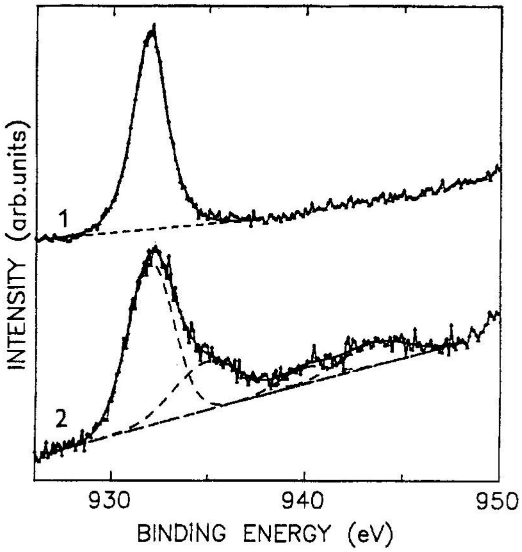

Fig. 2. The Cu 2p3/2 photoelectron spectra of $Cu_{12}Sb_4S_{13}$. Time of mechanical activation: 1 – 0 min, 2 – 30 min

can be supported by differences in copper and antimony leaching from the same tetrahedrite registered in our previous work (Havlik 1994).

In order to clear up the distribution of both elements in the surface of tetrahedrite, we applied the method of X-ray photoelectron spectroscopy. The Cu 2p2/3

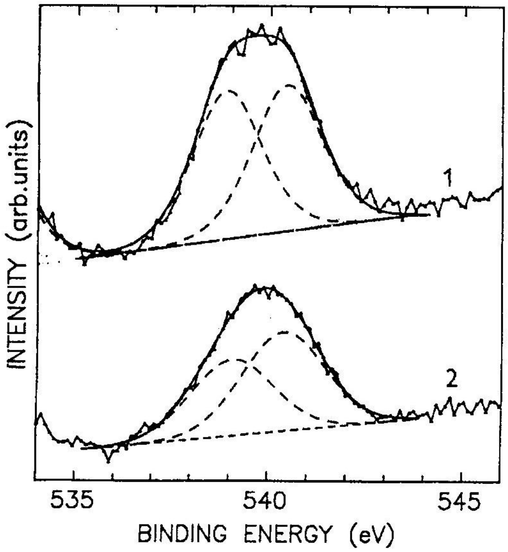

Fig. 3. The Sb 3d3/2 photoelectron spectra of $Cu_{12}Sb_4S_{13}$. Time of mechanical activation: 1 – 0 min, 2 – 30 min

and Sb 3d3/2 spectra of tetrahedrite are presented in Figs. 2 and 3. In the case of copper, the surface of the reference (i.e. non-activated) sample (Fig. 2, line 1) contains practically only Cu^{1+}. The mechanical activation leads, among others, to generation of the paramagnetic Cu^{2+} the presence of which is indicated by appearence of a satellite structure (Fig. 2, line 2 at binding energy exceeding 940 eV). The 3d3/2 antimony spectrum presented in Fig. 3 is a composition of two overlapping peaks. The lower binding energy peak corresponds to Sb in tetrahedrite while that for higher binding energy belongs to antimony oxide and/or antimony sulphate. The more intensive 3d5/2 antimony line cannot be used for identification of the antimony valence states because it overlaps the oxygen line. The intensity of the antimony peak with higher value of the binding energy is higher for mechanically activated sample (Fig. 3, line 2). In agreement with our results obtained by measuring the infrared spectra of mechanically activated sulphides (Balaž 1993) as well as with literature data (Nyquist 1971) we can deduce that the formation of oxide (Sb_2O_3 or Sb_4O_6) is more likely than that of sulphate.

The ratios of the atomic concentrations of copper and antimony were calculated with 10% error for quantitative determination of the distribution of both elements on the surface. The ratio Cu/Sb was equal to 1/0.66 for non-activated sample and to 1/1.34 for a sample mechanically activated for 30 min. The enrichment of the surface of mechanically activated tetrahedrite with antimony confirms the qualitative results obtained by the method of cyclic voltammetry.

The possibility of modifying the surface copper and antimony distribution by mechanical activation is a contribution for selective leaching of valuable metals from tetrahedrite. Our first results were published last year (Balaž and Braincin 1994; Balaž et al. 1994).

ACKNOWLEDGEMENT

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Za pomocą woltamperometrii cyklicznej i fotoelektronowej spektroskopii rentgenowskiej badano właściwości powierzchniowe tetraedrytu ($Cu_{12}Sb_4S_{13}$) aktywowanego mechanicznie w powietrzu. Stwierdzono, że mechaniczna aktywacja prowadzi do powstawania paramagnetycznych jonów Cu^{+2} w porównaniu do nieaktywowanego tertraedrytu, na powierzchni którego powstają jedynie jony Cu^{+1}. Zaobserwowano również wzbogacanie się powierzchni tetraedrytu w antymon.