

Mono-layer Compositional Analysis of Surface of Mineral Grains by Time-of-Flight Secondary-Ion Mass Spectrometry (TOF-SIMS)

TOF-SIMS를 이용한 광물 표면의 단층조직 분석 연구

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ABSTRACT : Although the bulk composition of materials is one of the major considerations in extractive metallurgy and environmental science, surface composition and topography control surface reactivity, and consequently play a major role in determining metallurgical phenomena and pollution by heavy metals and organics. An understanding of interaction mechanisms of different chemical species at the mineral surface in an aqueous media is very important in natural environment and metallurgical processing. X-ray photoelectron spectroscopy (XPS) has been used as an ex-situ analytical technique, but the material to be analyzed can be any size from 100 μm up to about 1 cm. It can also measure mixed solids powders, but it is impossible to ascertain the original source of resulting x-ray signals where they were emitted from, since it radiates and scans the macro sample surface area. The study demonstrated the ability of TOF-SIMS to detect individual organic species on the surfaces of mineral particles from plant samples and showed that the TOF-SIMS techniques provides an excellent tool for establishing the surface compositions of mineral grains and relative concentrations of chemicals on mineral species.

Key words : surface composition, surface reactivity, sulphide minerals, XPS, TOF-SIMS

요약 : 금속제련공학 및 환경과학 분야에 있어서 물질전체를 구성하고 있는 화학적 조성이 중요한 요소이나, 입자 표면의 화학조성과 미분화된 입자들의 표면 반응성을 제어함과 동시에, 입자 계면에서 일어나는 중금속과 유기물질등의 반응은 제련공정과 환경오염에 중요한 역할을 한다. 그러므로, 수용액상에 존재하는 여러 종류의 화학 물질과 광물입자 표면 사이에서 일어나는 계면반응 과정의 이해는 상당히 중요한 것이다. 일반적으로 입자 표면 분석에는 ex-situ 법을 사용하는 X-ray photoelectron spectroscopy (XPS) 분석 방법이 많이 적용되고 있으나, 이는 분석대상시료의 크기가 보통 100 마이크로론에서 1 cm 정도의 범위 안에 혼재-혼합되어있는 고체 입자들을 분석하기 때문에 채취

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분석된 X-ray의 원래 발산한 입자표면을 분석할 수는 없다. 그래서 본 연구에서는 Time-of-Flight Secondary-Ion Mass Spectroscopy (TOF-SIMS)를 응용하여 황화광물의 부유선광 공정 중 생성된 미세한 유화광물입자(30~75 microns) 표면에 형성된 무기, 유기물의 반응 관찰을 통해 이들의 정성분석 및 상대적 정량분석법을 연구하고자 하였다.

주요어 : 광물입자 표면, 개면반응, XPS, TOF-SIMS, 황화광물

Introduction

Although bulk composition and liberation are key considerations for mineral processors, surface composition and topography control surface reactivity and, consequently play a major role in determining flotation behaviour of minerals, since edges and dislocations are preferred sites for physico-chemical reactions. Surface properties play an essential role in many aspects of mineral processing. An understanding of interaction mechanisms of different reagents and species at the mineral-water interface is very important in achieving the selective flotation. However, the determination/characterization of mineral surfaces before and after treating with reagents is one of the most challenging tasks.

Spectroscopic measurements can provide a better understanding of mineral surface composition and hence the interactions between mineral-water and mineral reagents. There is a number of spectroscopic techniques that can be applied to study the surface chemical and elemental analysis (Brinen *et al.*, 1993; Chryssoulis *et al.*, 1994).

In-situ Fourier Transform Infrared (FTIR) measurements have been used for characterizing adsorption on mineral surfaces. Infrared spectroscopy, in general, provides information about the chemical bonding and molecular structure of organic and some inorganic materials on the surface, thereby permitting the identification of substances from the chemical and crystalline aspects. This technique is, however, not sufficiently sensitive for samples from mineral processing plants where adsorption concentration is low. Further, individual mineral grains in mixed mineral powders are almost impossible to investigate.

One ex-situ type analytical technique, X-ray photoelectron spectroscopy (XPS) is also available. For this technique the minerals to be analyzed can be of any size from 100 μm up to about 1 cm. It can also handle mixed mineral powders but it is impossible to ascertain the source of a given species, for example Pb signal from galena versus Pb from the surface of sphalerite. XPS surface analysis provides information on both elemental identity and chemical bonding. This information can be used to determine the chemical state of elements. Standardless semi-quantitative surface analysis, in atomic percent can be obtained with this technique. A significant number of XPS studies have been published in characterizing mineral surfaces, interaction between ions or collectors with minerals (Chryssoulis *et al.*, 1992; Cormia, 1992; Giesekke, 1983) in single mineral system.

Two complementary micro-beam techniques, laser ionization mass spectrometry (TOF-LIMS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS), have been successfully applied for the detection of organic and inorganic species such as activators on sphalerite, galena and pyrite particles (Marabini *et al.*, 1993), elemental mapping of inorganic species on sphalerite (Page and Hazell, 1989), hydrophobic flotation collectors and their molecular distributions on the surface of galena particles (Somasundran and Kunjappu, 1988). It was observed by Brinen *et al.* that the adsorption of dithiophosphate on galena surfaces is not uniform, which is in an agreement with the findings of previous works (Marabini *et al.*, 1993; Page and Hazell, 1989) of the present authors.

Micro-beam techniques with a small analytical spot size, 2~5 μm , are preferred in studying mineral surfaces, since in most mineral proc-

essing plants the majority of the particles are less than about 75 μm and in many cases less than 37 μm . Imaging of mineral surfaces for inorganic species is well established but is less developed for organics, primarily due to sensitivity considerations. With the use of a micro-focused liquid metal ion gun it is possible to map the distribution of elements as well as organic molecules such as collectors on mineral surfaces.

TOF-SIMS has several advantages over other surface analytical techniques. In this technique the particle surface is bombarded with a beam of ions and the surface species are sputtered off, producing mostly neutrals but also ions of positive or negative charge, which are analyzed in a time of flight (TOF) drift tube and detected by a sensitive detector. The action of the ion beam continuously erodes the sample surface in x-y-z direction removing successively deeper layers with increasing sputtering time. Because of the low primary ion current applied in the sputtering, a large proportion of the sputtered species is molecular in nature, both fragmented and parent. This feature is exploited to detect unfragmented radicals of hydrophobic collectors adsorbed on mineral particles. By rastering with the primary ion beam over a predetermined area on a single particle or a group of particles, elemental and molecular distribution maps are obtained. From these maps the homogeneity of surface coatings is established easily on a qualitative basis.

Furthermore, TOF-SIMS is the preferred technique for inorganic surface analysis of mineral particles because during the ablation/ionization processes essentially all molecular species are dissociated giving mass spectra free of molecular interferences, therefore easy to interpret. The application of TOF-LIMS for analyzing the surface of mineral particles has been reported elsewhere (Marabini *et al.*, 1993; Page and Hazell, 1989).

In this paper the mapping and the distribution of inorganic species on the surface of sulphide minerals (sphalerite, pyrrhotite and pyrite) from

plant samples and organic species on sphalerite and galena treated with activators and collectors are discussed. The study demonstrated the ability of TOF-SIMS to detect individual organic species on the surfaces of mineral particles from plant samples and shows that the techniques provides an excellent tool, complementary to the time-of-flight laser-ionization mass spectrometry (TOF-LIMS), for establishing the surface compositions of mineral grains and relative concentrations of chemicals on mineral species.

Experiment

Sample Preparation

Two sets of samples were used for the present TOF-SIMS work: samples from a mineral processing plant and specimen grade mineral samples. Samples from plant are deslimed on site with a 37 μm screen (400 mesh) using water from the same stream. Prior to drying, the plant water is displaced by distilled water to avoid surface contamination by dissolved species present in the plant water. The samples are then dried under vacuum and placed in glass vials, previously purged with nitrogen, and stored at -15°C to preserve the surface composition.

Sphalerite and galena particles from +99% pure specimens from Ward's Natural Science, freshly ground and deslimed (+37~75 μm size fraction) were treated with collector solutions of potassium amyl xanthate, and sodium di-isoamyl dithiophosphate at natural pH for 5-minutes and rinsed three times with distilled water to remove any remaining solution from the mineral grains. The collector concentrations used were 2×10^{-5} mol/g of solids, corresponding to approximately 50 times plant concentration levels. The sphalerite was activated with copper ions prior to conditioning with collectors.

Individual liberated mineral particles were identified under a stereoscope and picked up by using the tip of a tweezer and placed on indium foil immediately before the analysis. Since a particle can be viewed in its entirety, only lib-

Table 1. Analytical conditions for instrument

Cs gun (spectroscopy)	Primary ion energy	8 KeV
	Angle of incidence	60 to sample normal
	Ion pulse width	~1 ns
	Neutralizing electron energy	0...70 eV
	Pulse repetition rate	5 kHz
	Ions/pulse	~250
	Analytical area (μm)	200
	Ion dose (ions/cm ²)	>1013
Vacuum	$\sim 3 \times 10^{-9}$ Torr	
Ga LMI gun (Imaging)	Primary ion energy	25 KeV
	Angle of incidence	60° to sample normal
	Ions/pulse	~131
	Ion pulse width	100 ns
	Beam diameter	~0.3 μm
	Neutralizing electron energy	0...70 eV
	Pulse repetition rate	10 kHz
	Ion dose (ions/cm ²)	>1013
Vacuum	$\sim 3 \times 10^{-9}$ Torr	

erated grains were placed in order to analyze homogeneous grain surfaces. Indium as a substrate has the advantages of being both sticky and conductive.

Instrumentation

The TOF-MS instrument used is the PHI7200 manufactured by the Physical Electronics Division of Perkin Elmer. This instrument is equipped with two primary ion sources, the Cs gun for high mass resolution spectroscopy and gallium liquid metal ion gun for imaging and lower mass resolution spectroscopy. Analytical conditions for both ion guns are given in Table 1.

The surface composition of mineral particles ranging in size from 20 to 100 micrometers was established by probing a spot or by rastering a pre-selected area with analytical micro-beam size of 2~5 μm . The surface layers are sputtered off and the resulting positive and negative ions as well as the fragmented and parent molecules are analyzed. The analytical depth resolution is sub-monolayer.

Organic collector, amyl xanthate on sphalerite and galena, from laboratory treated samples were detected and their distribution was mapped. This source was used as the baseline data in the sub-

sequent analysis. Heavy metals, namely copper, lead, zinc and iron, and oxidation products on several mineral species were detected and mapped. The presence and population of specific organic and inorganic species on certain mineral particles are elucidated for their behaviour in metallurgical processing.

Data presentation is in the form of positive or negative ion mass spectra and in the form of maps showing the distribution of elements or organic molecules. Parent molecular ions were used to identify the organic species.

Result and Discussion

Inorganic Mappings of Mineral Surfaces of Plant Sample

The surface maps showing the distribution of selected positive ions on sphalerite, pyrrhotite, pyrite and quartz grains separated from the zinc concentrate produced at a plant were are given in Figs. 1~4, respectively. The topographic effect is obvious, but the uneven distribution of both positive (ea. Ca) ions are apparent. In Fig. 1, the zinc signal intensity is lower compared to that of iron, even though the grain is a sphalerite particle. This is most likely due to: (i) zinc

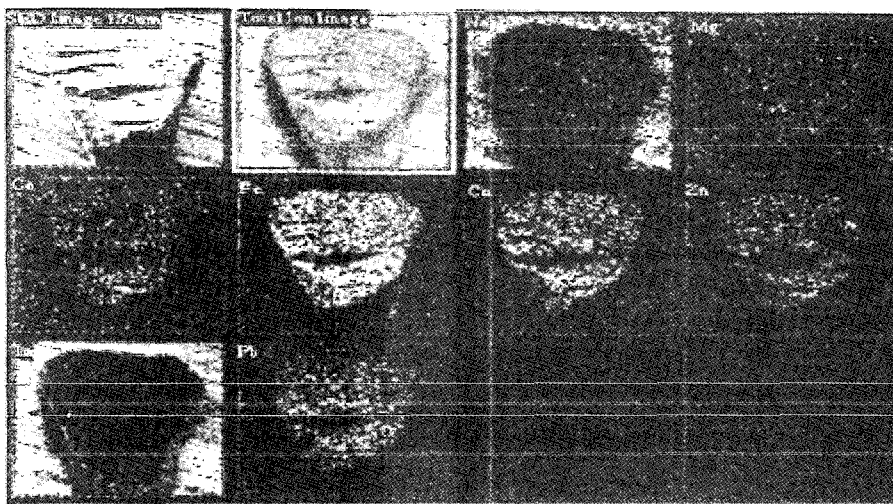


Fig. 1. TOF-SIMS positive ion maps of a sphalerite grain floated in the zinc concentrate.

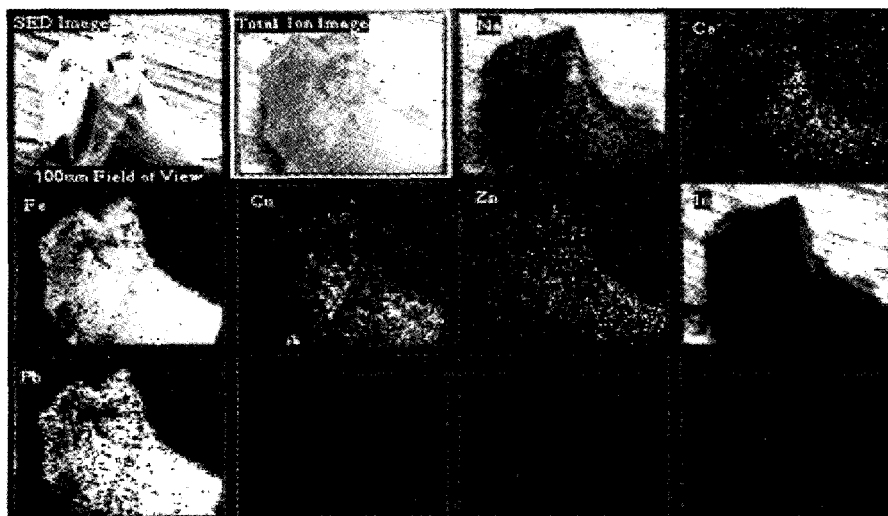


Fig. 2. TOF-SIMS positive ion maps of a pyrrhotite grain floated in the zinc concentrate.

has approximately ten times lower ion yield relative to iron, (ii) the surface layer of sphalerite became enriched in iron during grinding operation, and (iii) some surface zinc had been replaced by copper and/or lead ions at the surface level. The sphalerite particle in Fig. 1 appears to be activated with primarily copper and to a lesser extent with lead ions.

The positive ion maps of pyrrhotite, given in

Fig. 2, show differences in the distribution of cations. Copper is concentrated along the edge in the center of the particle, but also on the concoidal fractured surface. Lead ion is more or less uniformly distributed within the same surface regions where calcium is high, copper and zinc are lower. The pyrrhotite particle depicted in Fig. 2 has high lead population than copper on the surface indicating that it is more acti-

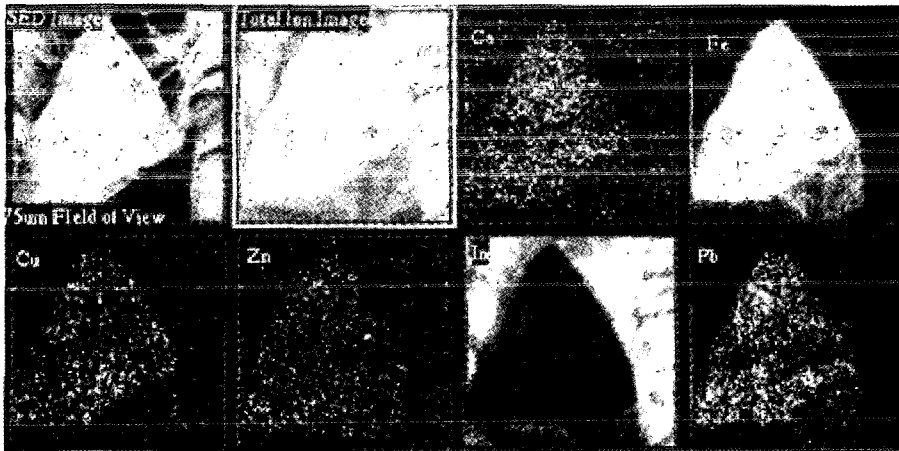


Fig. 3. TOF-SIMS positive ion maps of a pyrite grain floated in the zinc concentrate.

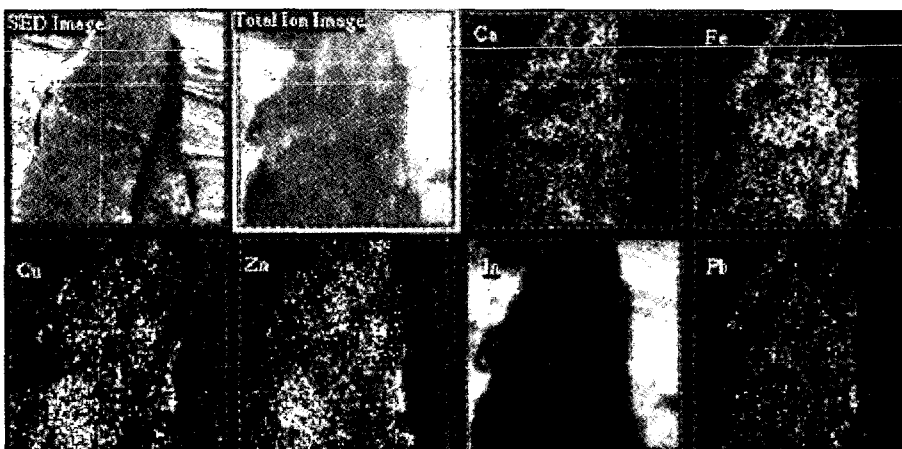


Fig. 4. TOF-SIMS positive ion maps of a quartz grain floated in the zinc concentrate.

vated by lead than copper.

The positive ion maps of pyrite in Fig. 3 show homogeneous distribution of calcium, copper zinc and lead. This pyrite particle floated into the zinc concentrate because of activation by copper and lead ions. Maps of quartz floated in the zinc concentrate (Fig. 4) show significant distribution of heavy metals on the surface as well.

Although the flotation conditions were adjusted to float only sphalerite in the circuit, small amount of other mineral species were also floated. Unwanted but the floated particles of pyrrhotite, pyrite and quartz are coated (acti-

vated) by available heavy metals. The source of the activating lead is the galena. The mill feed ore has about 0.2% Pb as galena. Activation by lead has been documented on numerous concentrators milling Cu-Pb-Zn sulphide ores and discussed previously (Marabini *et al.*, 1993; Page and Hazell, 1989).

Mapping of Amyl Xanthate Collector on Surfaces of Sulphide Minerals

Amyl Xanthate

Amyl xanthate was detected by TOF-SIMS on

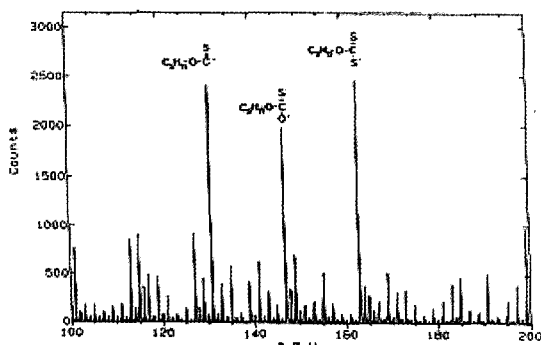


Fig. 5. TOF-SIMS negative ion mass spectra from surface of Cu activated sphalerite treated with potassium amyl xanthate.

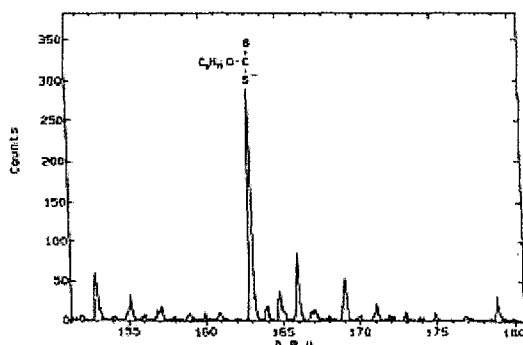


Fig. 6. TOF-SIMS negative ion mass spectra from surface of galena treated with potassium amyl xanthate.

the surface of galena and Cu-activated sphalerite grains. The negative mass spectra shown in Fig. 5 and 6 are from a sphalerite and galena particles, respectively. As shown in Fig. 5, there are three prominent peaks in the 100~200 amu (atomic mass unit) mass range for sphalerite. The peak at 163 amu represents the parent amyl xanthate radical (A-X⁻), while the intermediate peak at 147 amu is derived by the substitution of one sulphur atom with an oxygen atom. The third peak is a fragment ion of amyl xanthate having one S atom only. The negative ion mass spectrum for galena has only one prominent peak at 163 amu (Fig. 6), indicative of limited fragmentation resulting in great sensitivity to amyl xanthate.

Iso-amyl Dithiophosphate on Galena

Negative ion maps of the dithiophosphate radical and two of its fragment ions on a flat galena surface are shown in Fig. 7. The area imaged is about $15 \times 20 \mu\text{m}$. Adsorption of amyl dithiophosphate is linked to the crystallographic orientation of the galena substrate. This is evident not only from the distribution of the A-DTP⁻ radical but also from the distribution of its two fragment ions. Diagonally running strips of interchanging high and low concentration can be seen in all three maps. Furthermore, within a strip, localized high concentrations are also present. The width of the strips is 2 to 5 μm . It appears that where there is a high concentration

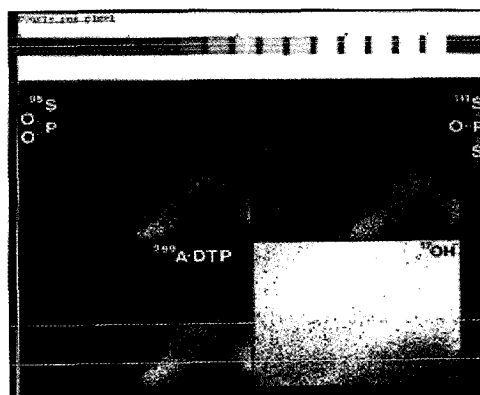


Fig. 7. TOF-SIMS negative ion maps of a galena particle treated with sodium di-isoamyl dithiophosphate.

hydro-oxyl groups on the surface there is less A-DTP⁻.

Conclusions

TOF-SIMS has been used successfully in detecting organic and inorganic species, and for mapping their surface concentration distribution on a number of sulphide minerals from laboratory as well as plant samples. The adsorbed species on the mineral particle surfaces can be detected and characterized by the presence of parent radicals and fragmented ions of the organic reagents. The "coating" of cations and hence collector adsorption on the sulphide mineral grains were found to be localized and non-

uniform. The characteristic fragment ions appear to be different between reacting sulphide mineral even with same collector type.

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