

XPS AND SEM OF UNPOLISHED AND POLISHED FeS SURFACE

RENTGENSKA FOTOELEKTRONSKA SPEKTROSKOPIJA IN VRSTIČNA ELEKTRONSKA MIKROSKOPIJA NEPOLIRANE IN POLIRANE POVRŠINE FeS

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It was attempted to measure parameters of Fe 2p and S 2p transitions for Fe and S in FeS to compare them with range of values obtainable from the literature. FeS specimen was manufactured from the standard material used for chemical analysis. X-ray Photoelectron spectroscopy (XPS) was first performed on non-polished and then on polished surface. Scanning Electron Microscopy (SEM) was used to image both surfaces. It was found that major constituents of non-polished surfaces are sulphate and sulphite compounds but that composition and structure of the polished surface are also complex and may become increasingly so after cleaning by ion sputtering. At best, composition of the surface approximated FeS very poorly, thus necessitating the use of literature Fe 2p and S 2p parameter values instead of directly measuring improved values.

Keywords: iron sulphide, FeS, XPS, SEM, ion etching, surface active element

Poskusili smo izmeriti parametre prehodov Fe 2p in S 2p za Fe in S v FeS, da bi jih primerjali s širokim razponom vrednosti iz literature. Vzorec FeS za meritve smo izdelali iz standardne kemikalije, ki se uporablja v kemijski analitiki. Z rentgensko fotoelektronsko spektroskopijo smo najprej opravili meritve na nepolirani in potem še na polirani površini vzorca. Z vrstično elektronsko mikroskopijo smo upodobili obe površini. Ugotovili smo, da nepolirano površino v pomembnem delu sestavljajo sulfati in sulfiti, da pa sta tudi sestava in struktura polirane površine kompleksni in da to kompleksnost čiščenje površine z ionskim jedkanjem lahko še poveča. V najboljšem primeru je sestava površine zelo slab približek za FeS, in je bolje še naprej uporabljati literaturne vrednosti za ustrezne parametre za Fe 2p in S 2p namesto direktno izmerjenih na obravnavanem vzorcu.

Ključne besede: železov sulfid, FeS, rentgenska fotoelektronska spektroskopija, vrstična elektronska mikroskopija, XPS, SEM, ionsko jedkanje, površinsko aktivni elementi

1 INTRODUCTION

Sulphur and its compounds appear in several of our recent and current research topics. It was found to be present in sulphide form in inclusions or oxide layers on austenitic stainless steels¹⁻³ or electrical steels⁴⁻⁶, in minute quantities as sulphate after electrochemical treatments of metals^{2,3,7-10}, and as surface active segregant facilitating surface reconstruction¹¹. In most of the above studies surface sensitive techniques have been extensively used¹²⁻²⁰, X-ray photoelectron spectroscopy (XPS) among them. In literature rather wide ranges of binding energies for characteristic transitions corresponding to S in sulphides, especially in FeS are reported^{23,22}. Part of the cause for the reported discrepancies may be in different experimental set-ups with variations in instrumentation and experimental parameters. Therefore an attempt to measure these values on the instrument used for all other XPS measurements in our recent and current studies was considered worthwhile. To this purpose a specimen was manufactured in two different ways from pure FeS used for chemical analysis. While variety of surface compounds was expected for the unpolished specimen the polished surface still did not yield predominantly FeS species corresponding to the

bulk of the specimen. With prolonged ion sputtering it developed a local surface reconstruction, thus hinting at fundamental surface unhomogeneity and at unsuitability of a bulk specimen as an XPS standard.

2 EXPERIMENTAL

Area of approximately $12 \times 9 \text{ mm}^2$ flattened by grinding at the top of a bulk specimen of FeS of approximately 5 mm thickness was investigated by SEM and XPS. This flat area was then polished down to 1 μm and investigations repeated. FeS was standard compound of molecular mass 87.92 (= 55.85(Fe) + 32.07(S)), used for chemical analysis. Unpolished and polished sample were cleaned by ion sputtering using Ar^+ at 3 keV, 1 μA , over $4 \times 4 \text{ mm}^2$ area. Estimated sputtering rate at these parameters is of the order of 1 nm / min^{23,24}.

SEM imaging as well as XPS of the sample were performed by VG-Scientific Microlab 310F SEM/AES/XPS. For all XPS measurements $\text{Mg K}\alpha$ radiation at 1253.6 eV with anode voltage \times emission current = 12.5 kV \times 16 mA = 200 W power was used. Beneficial carbon contamination at 284.8 eV C 1s binding energy (BE) was used to calibrate the binding energy scale. High resolution windows were measured around C 1s Fe 2p and S

2p transitions. Channel widths of 1 and 0.1 eV were used for survey and high resolution measurements. Several consecutive measurements were averaged to improve signal to noise ratio in high resolution measurements. XPS spectra were acquisitioned using Avantage 3.41v data acquisition & data processing software supplied by the SEM/AES/XPS equipment manufacturer. Casa XPS software²⁵ was also used for post-acquisition data processing.

3 RESULTS AND DISCUSSION

In **Figure 1** SEM images of unpolished and polished sample are shown.

Surface of the unpolished sample is heavily corrugated with corrugation amplitude up to several μm (**Figure 1a**), while surface of the polished sample is much smoother with maximum corrugation amplitudes below 1 μm (**Figure 1b**), which is consistent with the type of polishing applied.

Facet-like structure on the part of the surface visible in **Figure 2** but not in **Figure 1** suggests that surface reconstruction due to the ion etching and/or surface active element may have occurred. The fact that it only affects part of the surface may be due to the inhomogeneity of the surface

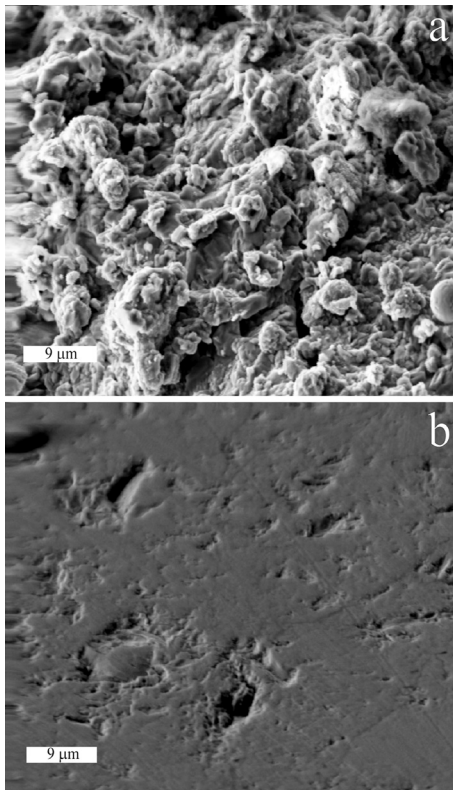


Figure 1: SEM images of unpolished (a) and polished (b) FeS specimen

Slika 1: Površina nepoliranega (a) in poliranega (b) vzorca FeS upodobljena z vrstično elektronsko mikroskopijo

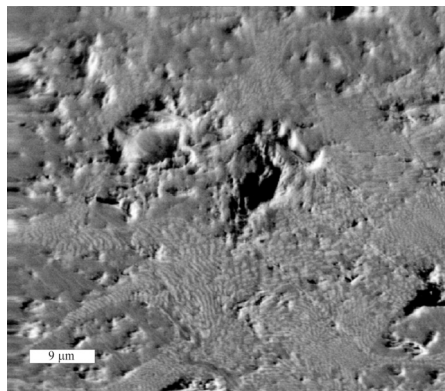


Figure 2: SEM image of polished specimen after 8100 s of sputtering
Slika 2: Površina poliranega vzorca po 8100 s ionskega jedkanja upodobljena z vrstično elektronsko mikroskopijo

In **Figure 3** high resolution XPS scans around S 2p, Fe 2p_{3/2} and O 1s on unpolished and polished surface after 300 s of sputtering are shown. Different components corresponding to different chemical states of S, Fe and O were used in fitting. They are listed in **Table 1**.

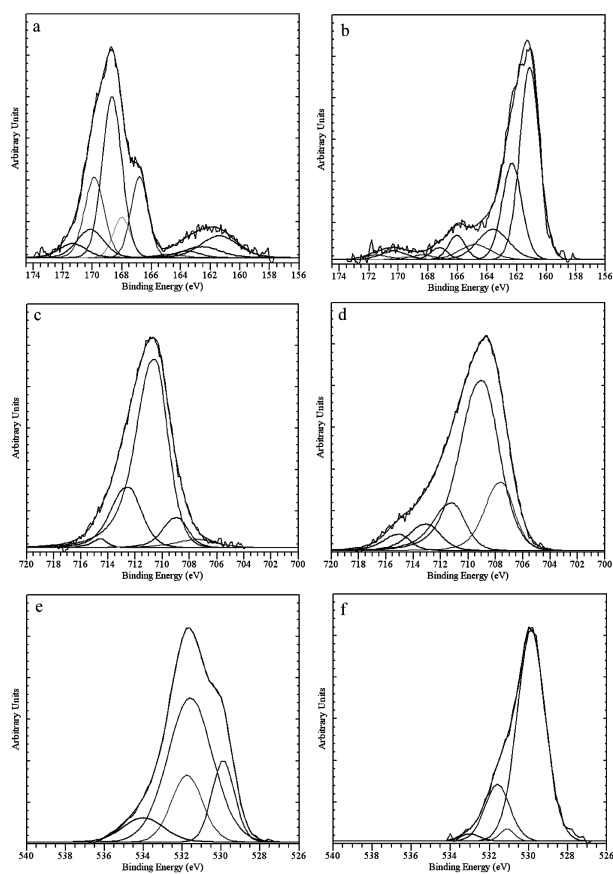


Figure 3: High resolution XPS scans around S 2p (a, b), Fe 2p_{3/2} (c, d) and O 1s (e, f) on unpolished (a, c, e) and polished (b, d, f) surface after 300 s of sputtering

Slika 3: Visokoločljive meritve z rentgensko fotoelektronsko spektroskopijo okoli 2p (a, b), Fe 2p_{3/2} (c, d) in O 1s (e, f) na nepoliranem (a, c, e) in poliranem (b, d, f) vzorcu po 300 s ionskega jedkanja

Table 1: S 2p, Fe 2p_{3/2} and O 1s components used in fitting High resolution XPS scans shown in **Figure 3**

Tabela 1: Komponente S 2p, Fe 2p_{3/2} in O 1s, ki smo jih uporabili pri fitanju meritev iz **Slike 3**

component	BE / eV	FWHM / eV
S (S ⁰) 2p _{3/2}	163.6 ± 0.2	2.5 ± 0.2
S (S ⁰) 2p _{1/2}	164.8 ± 0.2	2.5 ± 0.2
S (S ²⁻) 2p _{3/2}	161.1 ± 0.2	1.6 ± 0.2
S (S ²⁻) 2p _{1/2}	162.3 ± 0.2	1.6 ± 0.2
S (SO ₃ ²⁻) 2p _{3/2}	166.0 ± 0.2	1.3 ± 0.2
S (SO ₃ ²⁻) 2p _{1/2}	167.2 ± 0.2	1.3 ± 0.2
S (SO ₄ ²⁻) 2p _{3/2}	168.4 ± 0.2	1.9 ± 0.2
S (SO ₄ ²⁻) 2p _{1/2}	169.6 ± 0.2	1.9 ± 0.2
S (CHSO) 2p _{3/2}	170.3 ± 0.2	2.0 ± 0.2
S (CHSO) 2p _{1/2}	171.5 ± 0.2	2.0 ± 0.2
Fe (Fe ³⁺) 2p _{3/2}	711.0 ± 0.3	2.0 ± 0.3
Fe (Fe ²⁺ - S) 2p _{3/2}	707.1 ± 0.3	1.7 ± 0.3
Fe (Fe ²⁺ - O) 2p _{3/2}	708.7 ± 0.2	2.9 ± 0.2
Fe (Fe ³⁺ - SO ₄) 2p _{3/2}	712.7 ± 0.2	2.1 ± 0.3
[Fe (Fe ²⁺ - O) 2p _{3/2}] _{sat}	714.7 ± 0.2	1.7 ± 0.2
O (SO ₄ ²⁻) 1s	532.0 ± 0.4	1.5 ± 0.3
O (SO ₃ ²⁻) 1s	531.0 ± 0.4	1.4 ± 0.4
O (Fe oxide) 1s	530.0 ± 0.3	1.4 ± 0.2
O (contamination) 1s	533.5 ± 0.3	1.5 ± 0.4

Individual components in **Table 1** as well as their parameters were identified with reference to previous published work of XPS measurements on Fe-S compounds^{21,26,27}. It is to be noted that on the average 10 – 20 % larger half-widths of the components compared to references^{26–28} are not unexpected, since those XPS spectra were measured using monochromated X-ray source. Significantly larger half-widths (of the order of 50 %) than in references were measured for components corresponding to S (S⁰) i.e. elemental sulphur and Fe (Fe²⁺ - O) i.e. iron in iron(II) oxide.

The first may be explained due to components characteristic of elemental sulphur and of polysulphides being very close in their binding energies to the point of virtual overlap, not being resolved into two components²⁷. The second is most probably an effect due to preferential sputtering of oxygen compared to iron which causes continuous change in binding energy of iron oxides.

In **Figure 4** results of sputter cleaning onto concentration of different types of surface compounds on the unpolished and polished specimen is shown. These types of compounds are classified as iron oxides, iron – sulphur compounds and sulphur – oxygen compounds. They were arrived at by summing concentrations of corresponding components (e.g. O (SO₃²⁻) 1s and O (SO₄²⁻) 1s for oxygen in sulphur – oxygen compounds). **Figure 4a** shows that majority of the unpolished surface consists of sulphates and sulphites and that their percentage remains significant even after intense cleaning by ion etching (6300 s). Another significant constituent are iron oxides that change even less with sputtering time. Probable reason for this is that 6300s of ion etching roughly corresponds to 0.1 μm of material etched off, in

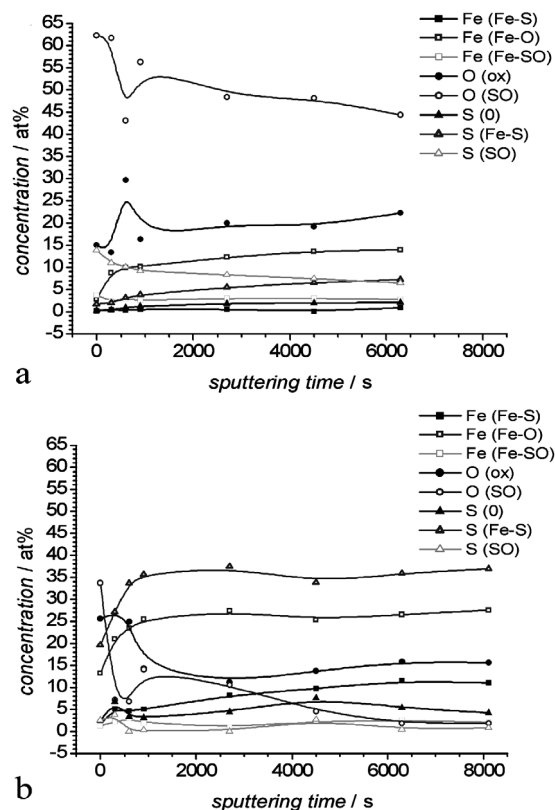


Figure 4: Main types of compounds on the surface during sputter-cleaning of the unpolished (a) and polished (b) specimen

Slika 4: Glavni tipi spojin na površini nepoliranega (a) in poliranega (b) vzorca med čiščenjem z ionskim jedkanjem

some areas even less due to shading effects of the highly corrugated surface with average corrugation amplitude of the order of several μm (**Figure 1a**).

Figure 4b shows that on the polished surface sulphates drop much faster than on the unpolished one, which additionally suggests that much of the highly corrugated surface structure on the unpolished surface

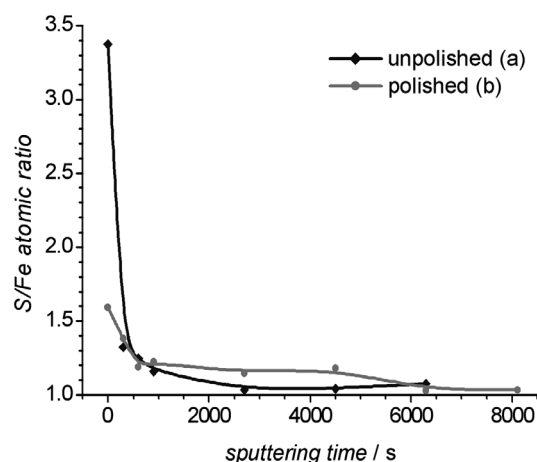


Figure 5: S/Fe atomic ratio with sputtering time for unpolished (a) and polished (b) specimen.

Slika 5: Atomsko razmerje S/Fe v odvisnosti od časa ionskega jedkanja za nepoliran (a) in poliran (b) vzorec

actually consists of sulphates. It can be also seen that there is more Fe and S corresponding to FeS than on the unpolished surface, though far from being the major components, but also lot of iron oxides and some elemental sulphur.

In **Figure 5** S/Fe atomic ratios with sputtering time for unpolished and polished specimen are shown. Initial values are rather high, they, however drop below 1.2 after first sputtering cycle and remains approximately constant in unpolished sample while in polished one it decreases somewhat further and approaches 1 towards end of the sputtering time. Even at this stage, with iron and sulphur atomic ratio close to 1, actual surface stoichiometry is much more complex as can be seen from **Figure 4**.

Real inhomogeneity of the surface, structural as well as compositional is best revealed by facet-like structure that appeared in small area of the polished sample after 8100 s of sputtering (**Figure 2**, compare to the same area in **Figure 1b** before sputtering). This structure is most probably induced by ion etching^{14,29–31}, but its appearance may also be enhanced by elemental sulphur acting as surface active element^{11,32}. If this is indeed the case, islands of the structural and compositional homogeneity over the surface of the polished and ion etched sample seem to be of the size of the order of micrometers.

4 CONCLUSIONS

Non-polished and polished flat areas on specimens manufactured from FeS were XPS profiled. Both surfaces were imaged by SEM. It was found that major constituents of non-polished surfaces are sulphate and sulphite compounds with slightly increasing iron oxides species concentration during the ion etching. In polished surface there is a fast drop of sulphate and sulphite compounds concentration accompanied by increasing iron oxides species concentration as well as iron sulphide and elemental sulphur concentrations. While S/Fe ratios for both types of specimen may reach approximately or virtually 1 during the ion etching, this is not due to the specimens' surfaces consisting (primarily) of FeS. Comparing SEM images of polished surface before and after profiling a localized facet-like surface reconstruction is revealed that may have been induced by combination of ion beam etching and elemental sulphur as surface active element. Localized nature of this surface reconstruction also suggests high surface unhomogeneity of the specimen. For some types of materials, especially for non-metallic ones, it may be necessary to prepare a useable standard for surface sensitive spectroscopy in a form of a thin film^{33–36}.

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