PROFILE ANALYSIS OF MICROPARTICLES

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Depth resolved analyses of several types of microparticles are presented. Particles for secondary ion mass spectrometry (SIMS) depth profile analysis were collected in the working environment of glass plant, steelworks and welding station using eight-stage cascade impactor with particle size range of 0.3 μm to 15 μm. Ion beam sputtering and sample rotation technique allowed to describe morphology i.e. the elemental structure of collected sub-micrometer particles. Also model particles Iriodin 221 (Merck) were depth profiled.

The core-shell structure is found for all types of investigated particles. Steelworks particles consist mainly of iron and manganese cores. At the shells of these microparticles: lead, chlorine and fluorine are found. The particles collected in the glassworks consist mainly of lead-zirconium glass cores covered by carbon and copper. Stainless-steel welding particles compose of iron, manganese and chromium cores covered by a shell rich in carbon, chlorine and fluorine. Sample rotation technique applied in SIMS appears to be an effective tool for environmental microparticle morphology studies.

Introduction

Nano and microparticles have very large surface to volume ratio and their properties may substantially differ from the bulk materials. They may remain suspended in air for a long time. Recently these particles have moved to the center of attention, because of their well-documented effect on public health. They are deposited in the alveoles of the lung, where the defence mechanisms of the human body are weak; in this way, a number of toxic chemicals adsorbed at the nanoparticle surface penetrate into the human body using the nanoparticles as vehicles.

The importance of particulate matter in the environment is well understood: particles are the major material carriers in water and in air, atmospheric aerosols influence visibility and the global climate and many components of environmental particles are toxic [1].

Sub-micrometer particles may be directly emitted (primary sources) or derived from chemical reactions occurring in the atmosphere (secondary sources), and undergo further chemical modifications as they age. Research efforts are focused also on working environment microparticles. The aim is to analyse their morphology, which can reflect the chemical processes as well as adsorption and condensation on the particle surfaces [2, 3]. Recently core-shell structure was found in industrial [4] and urban aerosol particles where both chromium and vanadium cover aluminosilicate cores [5].

In this study morphology of aerosol particles was measured with secondary ion mass spectrometry (SIMS) one of surface analytical methods [6]. As the analysed surface is sputtered away, observation of the distribution of the constituents with depth in particles and the compositional heterogeneities within particles is possible.

I. Experimental

The analysed material was respirable industrial microparticle dust collected in glass plant; steelworks and also in welding station using eight-stage particle impactor [7]. The airflow through the impactor was 6.8 l/min and total particle diameter range 0.3 - 15 μm. Rotating plates of impactor were used in order to get homogeneously covered carrier. To prevent particle charge build up during ion bombardment the sampling time in collection process was chosen to form monolayers of the particles with less than about 50% coverage of the carrier. Analysed particles were sub-micrometer (diameter range 0.3 – 0.4 μm) and were attached to indium substrates and introduced into vacuum for SIMS depth profile analysis on SAJW-02 apparatus equipped with Balzers 16 mm quadrupole spectrometer and sample rotation manipulator [8]. Sputtering was performed using ion guns with electron bombardment sources; 5 – 0.5 keV Ar^+ ion gun (Physical Electronics) and O_2^+ ion gun [9], with the beam incidence angle of 45° to the flat 0.3 mm diameter substrate, holding analysed particles. Scanning of 100-μm diameter beam was performed in the square range of 0.6 mm, i.e. wider than the substrate dimension, to avoid crater edges. Sample rotation around an axis perpendicular to the substrate at 1 rev/min was applied in order to minimise shadowing effects and get more uniform erosion conditions. The method is described in detail in [10].

As model particulate matter for depth profile analysis we used Iriodin-221 (Merck) composed of 5 – 25 μm "core-shell" particles, where the core is composed of illite and the shell is 425 nm thick layer of rutile (TiO_2). Bulk analysis of the sedimental microparticles was performed on spark source mass spectrometer SSMS JEOL JMS-01BM2 and X-ray diffraction on Siemens D-500.

II. Results

Prior to analysis of industrial contamination particles the analysis of model particles was performed. The results are shown on fig. 1. Ti^+ secondary ion emission represents rutile shell, while the illite core of particles emits Si^+ ions. After the removal of top layer of TiO_2, follows the erosion of the core and again the erosion of the bottom TiO_2 layer. Falling down signals at a depth over 1.5 μm shows so-called "consumption" of the sputtered particles attached to the indium substrate.

Industrial air pollution microparticles collected at several working stations do not show such clear structure as model particles. Collection of the material for analysis was performed in different industrial working areas. Total air pollution (particle diameter range 0.3 – 15 μm) in glass plant was in the range 0.06 to 1.3 mg/m^3, in steelworks 2.7 to 5 mg/m^3 and at welding station 1.4 to 11 mg/m^3. Pollution of 0.3 – 0.4 μm diameter class particles was: 0.6 – 0.03 mg/m^3 in glass plant, 2 – 0.5 mg/m^3 in steelworks and 2 – 0.2 mg/m^3 at welding station.

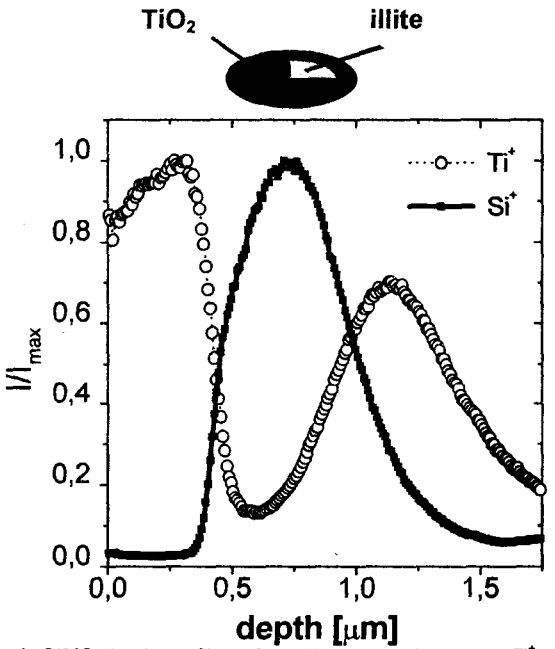

Fig. 1. SIMS depth profiles of positive secondary ions: Ti^+ and Si^+ emitted during ion bombardment of Iriodin 221(Merck) particles using the sample rotation technique. Iriodin particle model is shown above.

Bulk analysis of sedimentary samples of glass plant particles showed the presence of over 30 elements, the main being: Pb, Ba, Zr, Sr, Fe, Ca, K, Si, Al and Na. The composition is typically the glass, containing additionally some steel elements as well as copper. X-ray diffraction results confirm this result, showing that particulate material is generally amorphous with the addition of 1-% trace of quartz.

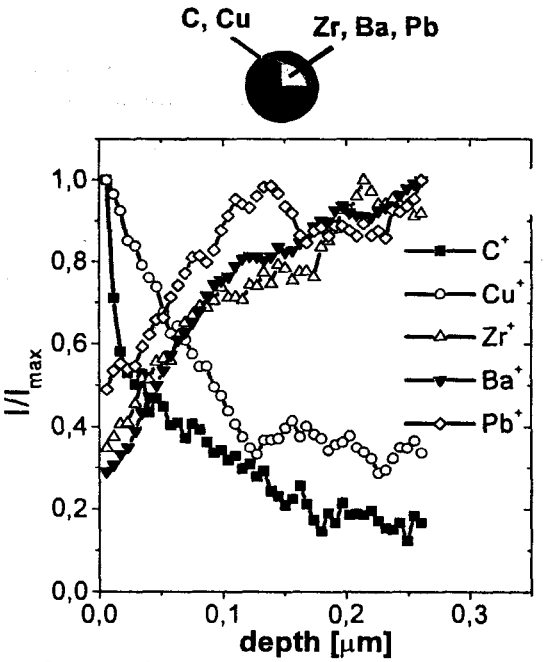

Fig. 2. Depth profile analysis of 0.6 - 1 μm particles collected in glass works. Above, morphology is shown schematically.

Analysed steelworks particles compose of 50 elements, mainly of carbon, iron, calcium and silicon and magnesium. X-ray diffraction shows that all samples collected in steelworks have polycrystalline structure with well-developed crystallites of graphite magnetite, hematite, crystobalite, periclase and quartz. [11]

Particle collection during gas tungsten arc welding and shielded metal arc welding shows that the majority of the particles is below 0.4 μm diameter size. Particles are composed of oxidised welding material as well as electrode material.

SIMS depth profile analysis was performed on particles of three classes (0.3 - 0.4 μm, 0.4 - 0.6 μm 0.6 - 1 μm). Initial stages of the sputtering process indicate what elements are present at the particle surface. Further sputtering causes the emission of the elements present mainly in the particle cores. Falling down signals of secondary ions relate to consumption of sputtered particle material.

Glass plant microparticle depth profiling example is shown on fig. 2. Registered are the signals of positive secondary ions of carbon, sodium, copper, zirconium, barium and lead. The falling down signals of carbon and copper, and in contrary rising up signals of lead, zirconium and barium in the range of 200 nm suggest that sub-micrometer particles have core-shell structure. We can conclude that the surface of lead-zirconium glass particles is partially covered by about 200 nm thick carbon and copper-containing layer. So the glass particles, suspended in working environment ambience, adsorb the other substances like carbon and copper contamination emitted by various technological sources. Effects of glass particle ion erosion are visible on fig. 3. Hollow indium surfaces around the particles were formed during sample rotation ion bombardment.

Fig. 3. Scanning electron microscope image of glass microparticles sputtered with sample rotation technique. Hollow surfaces in indium carrier surround the particles.

Particles collected in steelworks also do not have homogeneous morphology. The monitored elements were the major components of the particles as: iron, silicon and manganese and also the other constituents as: barium, copper, lead, chlorine, fluorine, zinc etc. Both positive and negative secondary ion currents were monitored. On fig. 4 are presented only

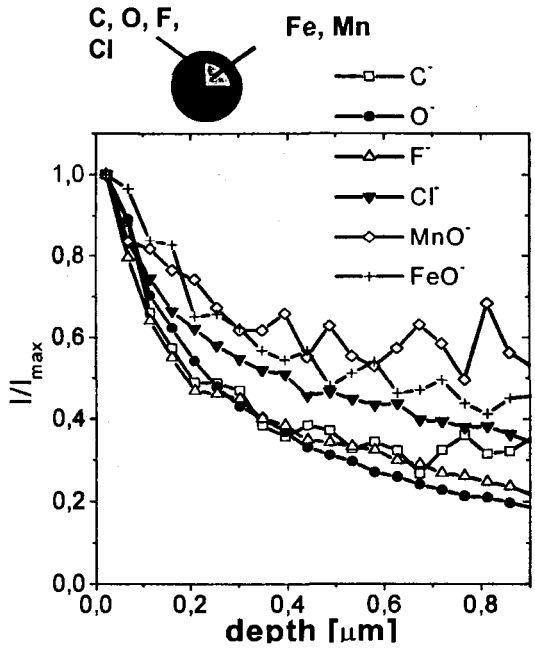

Fig. 4. SIMS depth profiles of negative secondary ions emitted during ion bombardment of steelworks 0.3 – 0.4 μm particles. Model of "core shell" particle is shown above.

the results of chosen negative ions. The initial stages of sputtering are accompanied with the rapid falling down of carbon, chlorine and fluorine signals, while iron oxide and manganese oxide signals fall down more slowly within the 50 - 150 nm depth ranges. This suggests that, chlorine, fluorine, carbon and oxygen are concentrated mainly at the particle surfaces. Further sputtering gives the gradual fall down of all signals due to the total "consumption" of bombarded particles. The obtained results of negative secondary ions for steelworks particles agree generally with the positive SIMS results. [11]

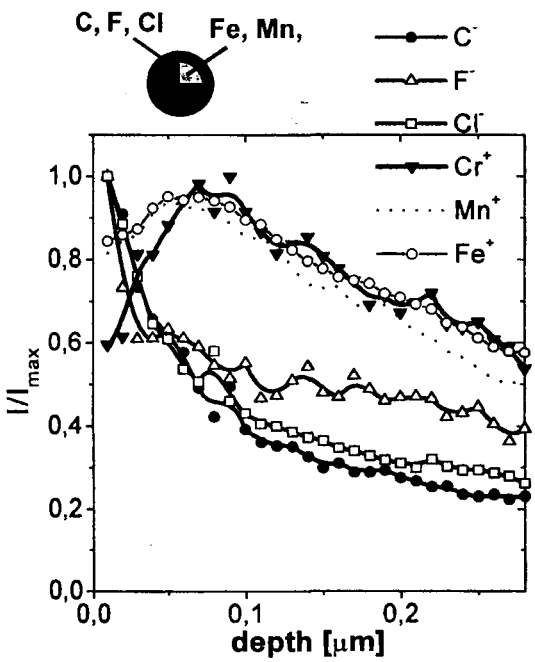

Fig. 5. Depth profile analysis of welding fume 0.3 – 0.4 μm particles. Model of "core shell" particle is shown above.

Both positive and negative secondary ion currents are shown for welding fume particles depth profiles (fig. 5). Particles of the class 0.3 – 0.4 μm, collected during stainless steel argon arc welding, also have "core – shell" morphology. Carbon, fluorine and chlorine are detected mainly at the shell layer 50 nm thick. The cores are composed of the main steel components as iron, manganese and chromium. However, it is visible, that manganese segregates towards the shell layer while chromium remains in the core.

Results of depth profile analyses of glass plant and steelworks particles [11] and welding fume are gathered in table 1.

Table 1.
Morphology of the industrial sub-micrometer particles collected by vacuum impactor in glass plant, steelworks (near mixer, converter and heavy-section mill) and in welding station during argon tungsten arc welding of stainless steel. Results of sample rotation SIMS are shown. The elements enriching the shells are specified as well as the elements dominating in the cores of particles.

Work station – microparticle class	Microparticle shell	Microparticle core
Glass Plant 0,6 - 1 μm	C, Cu	Pb, Zr, Ba
Steelworks - mixer 0,3 - 0,4 μm	Pb, Cl	Ti, Mg, Mn
0,4 - 0,6 μm	Pb, Cl, Mg, Si	Mn, Fe, Zn, Ba
converter 0,3 - 0,4 μm	Pb, F, Cl	Mn, Fe, Ca
0,6 - 1 μm	Pb, F, Cl, Si	Mn, Fe, Ba
heavy-section mill 0,3 - 0,4 μm	Pb, Cl, Si	Mn, Fe, Ca
Welding fume 0,3 - 0,4 μm	C, F, Cl	Fe, Mn, Cr

Depth resolved analysis show that most of the collected particles have core-shell structure. The results however do not present the strict difference between the cover and the core of the particles. Rather the enrichment of some elements in the shell layer is observed, while the major components are forming the core. Matrix effects also influence strongly secondary ion emission.

Conclusion

Presented results show that the sample rotation technique can be successfully applied to the depth profile analysis of non-flat layered structures. This technique can improve the accuracy of SIMS analysis, since in the case of constant azimuth angle bombardment, erosion of microparticles is not parallel to their surface. A more uniform erosion is obtained with the variable azimuth ion bombardment mainly due to reduction of the shadowing effect.

The application of sample rotation technique to depth profile analysis to working environment particles shows that the particles do not have uniform morphology. The shell-core structure has been observed for particles collected in all three cases. Presented models show that steelworks particles consist mainly of iron and manganese cores. At the shells of these microparticles: lead, chlorine and fluorine are found. The particles collected in the glass-works consist mainly of lead-zirconium glass cores covered by carbon and copper. Welding fume particles also have cores of different composition than their shells.

Application of the sample rotation in depth profile analysis opens new perspectives in research of toxic and carcinogenic substances absorbed at the surface of microparticles. Particle morphology research can explain many hazardous processes present in the working environment. The surface rather than a core or average composition give chemical behaviour of the particles for heterogeneous reactions. Thus development of surface analysis of micro and nanoparticles is needed for further numerous technological and environmental applications.

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