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First experiences on characterization of surface oxide films in powder particles by Glow Discharge Optical Emission Spectroscopy (GD-OES)

SPECIAL FEATURE

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The surface characteristics of the powder particles play a key role on the processing of the powders to consolidated products and on the final properties achieved for the material. Characterization of surface oxide films by techniques commonly used such as X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy provide reliable information on the surface films, but they are time-consuming methods and the analyzed areas are very limited. In this evaluation, the potential of the depth profile analysis by Glow Discharge Optical Emission Spectroscopy (GD-OES) is experimented for loose powder particles for the first time. Hitherto, the lack of a sample preparation technique has hindered the use of this powerful surface analysis technique for loose powder.

Introduction

Metal powders have a high affinity to oxygen and thus they are very reactive when coming into contact with air or other oxygen containing atmospheres/surroundings. A thin film of metal oxide is formed on the particle surface. Oxidation can occur whenever the material is exposed to oxygen for instance during the manufacturing, processing and handling of the powder. The characteristics of surface oxides are of vital importance in the processing of the powder to a final product as they contribute the properties of the product. Increased knowledge about the surface films is also highly useful for the optimization of the processes such as sintering or additive manufacturing [1,2].

X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) are commonly used for the characterization of surface oxides in powder materials. In these techniques, the surface of the powder particles is sputtered by energetic particles after which the surface remaining after erosion can be analyzed. The source of sputtering particles can vary from ion source, X-ray source, a plasma, an accelerator or other. The analytical performance such as later and depth resolution can significantly vary depending on the sputtering source. Electron microscopy on cross-sections of powder particles is also widely used for the surface characterization. Here, the analytical performance is mainly influenced by the interaction volume of the electron beam with the sample. The main drawbacks of the commonly used surface characterization methods are that they are time-consuming and the analyzed areas are limited to a modest amount of powder particles [1,3].

The analyzing technique making use of glow discharges coupled to optical emission spectrometry (GD-OES) is a well-established method for depth profile analysis of solid materials excluding powder materials. In this technique, a glow discharge is created by applying a voltage between the sample being a cathode and a tubular anode in a low-pressure gas. When the voltage exceeds a certain value, the gas ionizes into plasma and begins conducting electricity. As soon as the plasma is ignited, the surface of the sample material will be subjected to sputtering of the ions of the plasma. The sputtered material from the sample diffuses into the plasma, where it gets excited. The optical emission of the plasma is detected giving indication of the elements present in the sputtered material. The sputtering process is dependent on the properties of the sample, meanwhile the excitation process is essentially independent on the sample material. The fact that the excitation process and optical emission is independent of the sample, is the critical factor for an easy quantification of compositional information as a function of sputtering depth. This technique is called GD-OES depth profiling [3,4].

The technique is a powerful analytical tool for the direct analysis of solid samples. The advantages of it include ease of use, fast sputtering rate, high depth resolution, excellent

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sensitivity for low concentrations, multi-element capability, good quantification and high sample throughput. The aim of this work was to experiment a suitable sample preparation technique for analysis of loose powder by GD-OES and to analyze applicability of the tested method for the analysis of surface oxide films in powder materials [4].

Operational principle of GD-OES depth profiling

The glow discharge source commonly used in depth profiling consists of an anode tube and the sample to be analyzed. The source is generally named as Grimm type of glow discharge lamp, see Fig. 1 for an illustration. The flat sample is placed perpendicular to the front of the anode tube, which is kept at ground potential. Electrical power is supplied directly to the sample. A distance of about 0.1–0.2 mm is kept between the sample and anode tube. Sufficient vacuum tightness is achieved by an O-ring, which separates the discharge chamber from air environment [4].

When the plasma is ignited inside the plasma chamber, free electrons and plasma are generated. Both species will move freely in the electrical field controlling the plasma chamber and will influence the electrical field through creation of local charge distributions. Different characteristic areas are formed in the plasma. Two of them are fundamental for the use of the glow discharge for analytical purposes: the negative glow, free of electrical field but showing high charge density for both ions and electrons, and the cathode dark space. The latter attracts positive ions toward the cathode and generates the sample sputtering. The sputtering also sets free secondary electrons, which are accelerated in the electrical field toward the negative glow, where they lose their energy through collisions. During the collisions the secondary electrons participate in excitation and ionization processes and thus maintain the plasma [4].

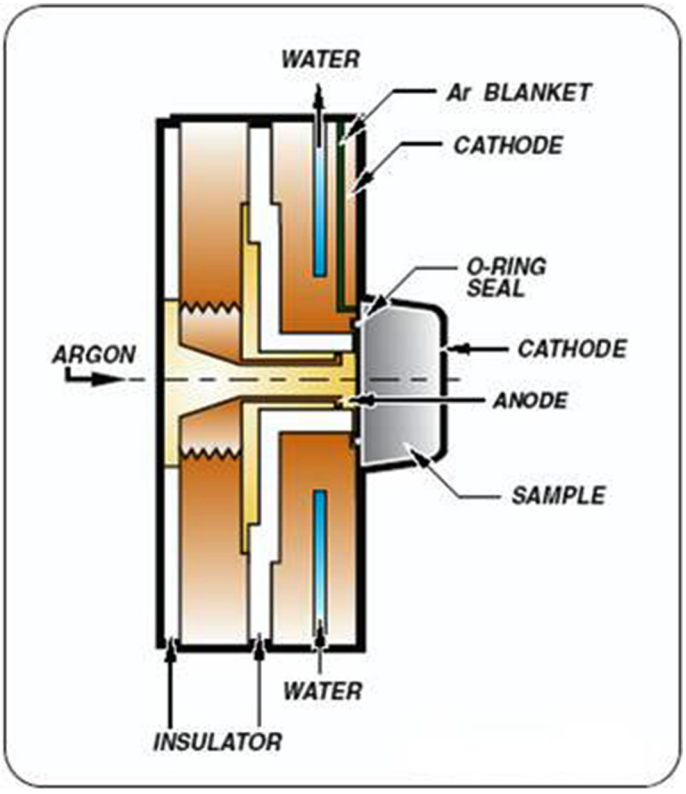

FIGURE 1
A schematic illustration of Grimm glow discharge source.

The sputtering process depends strongly on the sample material and its surface properties, but once the atoms are sputtered they move as single atoms into the negative glow. There they are diluted in the argon carrier gas. All the elements at the sample surface are sputtered at the same rate as soon as the equilibrium conditions for the plasma are achieved after the plasma ignition. Preferential sputtering of elements does not play a significant role as the sputtering ions have a rather low energy of 100 eV. Mixing of atomic elements during sputtering is very weak. The excitation and ionization process mainly occur in the negative glow. Ionization and excitation yields are independent of the properties of the sample, but however they are strongly element-specific. For emission processes they are even specific to each spectral line. The quantification of GD-OES signals is relative uncomplicated giving quantitative information of the content of several species. GD-OES is able to analyze surfaces varying from a few nanometers to 100 μm. The elemental concentrations range from 0.001% to 100% (mass fraction). The limitation of the technique is that it lacks lateral resolution. The analytical data is averaged over the area defined by the inner diameter of the hollow anode, typically 4 mm. Depending on the application this can be an advantage or disadvantage [4].

Experimental

Samples and sample preparation

The powder materials of this work included a water atomized Astaloy CrM and a gas atomized 316L material, see Table 1 for their nominal chemical composition provided by Höganäs AB Sweden and Carpenter Powder Products, respectively. The nominal oxygen content of the tested powders varied between 0.02 and 0.16 wt%. The studied size fraction of both the powders was 25–32 μm.

The samples were prepared by compacting powder against a solid metallic substrate in order facilitate the required vacuum tightness and the low distance of 0.1–0.2 mm between the anode and cathode for the Grimm glow discharge source. The adherence of the particles to the substrate was achieved through compaction. The press tool for the compaction had a very fine surface finish and a coating in purpose to prevent the transfer of surface films from the powder to the press tool by adhesive effects, see Fig. 2 for a SEM image displaying the compacted particles. As a final stage in the sample preparation, the compacted particles were coated with a 15 nm thick layer of gold in purpose to assist stabilization of plasma during the start of the measurement. The signals originating from the top coatings can be excluded in the computation of analysis results.

TABLE 1

The nominal chemical composition of Astaloy CrM and 316L powder (wt%).

Powder	Cr	Mn	Mo	Ni	Si	N	O	Fe
Astaloy CrM	2.96	0.10	0.48	–	0.03	–	0.16	Bal.
316L	16.83	1.42	2.10	10.58	0.52	0.13	0.02	Bal.