STUDIES OF OXIDE REDUCTION AND GAS ADSORPTION BY USING POSITRON ANNIHILATION SPECTROSCOPY

SØREN LINDEROTH
Materials Department
Risø National Laboratory
DK-4000 Roskilde
Denmark

ABSTRACT. Applications of positron annihilation spectroscopy to the study of surfaces of nano-particles and mesoporous solids are reviewed, especially the high sensitivity of positrons to gas adsorption is being stressed.

1. Introduction

The properties of nanophase materials are primarily governed by the large surface and interfacial regions of the nanoparticles comprising these materials, e.g. their chemical properties are determined by the composition and the structure of the particle surfaces, and a mechanical property such as superplasticity is an effect related to interfaces. Sintering reactions, self-diffusion and melting are other properties that have been found to differ considerably from those for bulk materials. These properties depend on, e.g., the structure of the interfaces and surfaces and on the presence of secondary phases such as oxide layers on the particle surfaces. Information about the structure of surfaces and interfaces as well as information about the presence of adsorbed gases and oxide phases is therefore a requisite for a better understanding of the properties of nanophase materials.

The task of obtaining information about the internal structure and the processes occuring in nanophase materials in not an easy one. Several experimental techniques are being used, e.g. x-ray and neutron diffraction, x-ray absorption fine structure (XAFS), Mössbauer, and the positron annihilation (PAS) spectroscopies. The techniques yield complementary information about, e.g., structure, defects, surfaces and gas adsorption in the nanophase materials.

In the following positron annihilation spectroscopy studies on oxide reduction and gas adsorption in nanophase materials and porous media will be reviewed. Such studies have only been performed quite recently. Positron annihilation spectroscopy has previously been utilized in the study of gas adsorption and desorption at the surfaces of voids and bubbles in metals [1]. Based on those results it was obvious to make attempts to also employ positron annihilation spectroscopy to the study of surfaces and interfaces of nano-particles [2-7], porous glasses [8] and exfoliated graphite [9-13]. Some of the advantages of positron annihilation spectroscopy is that i) positrons have
a large tendency to become trapped and annihilate from surfaces, i.e. the spectroscopy is selectively sensitive to surface phenomena, ii) studies may be performed in vacuum as well as in gas at different densities and temperatures, and iii) the technique can yield information about the (defect) structure at interfaces. To facilitate the understanding of the experimental results, aspects of the positron annihilation spectroscopy will be reviewed briefly in the following paragraph.

2. Positron Annihilation Spectroscopy

Positrons (anti-electrons) are created by a nuclear decay, e.g. by the decay of $^{22}$Na. The positron is in this case emitted with an average kinetic energy of about 180 keV, which is sufficient for the positron to penetrate to an average distance of tens of $\mu$m in metals [14]. In the investigated sample the positron thermalizes within a few picoseconds whereafter it performs random walk with an average diffusion length of about 100 nm. In defected materials the positron may enter a localized trapped state, e.g. the positron may become localized in a mono-vacancy or at the internal surface of a void or bubble. The life of the positron ends by annihilation together with one of the surrounding electrons; the two particles being transformed into gamma radiation. The radiation is mostly emitted as two $\gamma$-quanta, each with an energy of 511 keV [15,16].

Several techniques, based on the measure of the positron-electron annihilation characteristics, have been developed [15,16]. One technique is the positron lifetime technique where the positron lifetime in the investigated material is measured by detecting the time difference between a $\gamma$-quantum emitted at the same time as the positron is 'born' and one of the annihilation quanta. By another technique (the so-called Doppler broadening technique [15,16]) the energy distribution of the annihilation $\gamma$-quanta is measured. The positron annihilation rate is determined by the overlap of the positron wave function with that of the surrounding electrons. As this overlap is different in different positron states both the positron lifetime and the energy distribution of the annihilation gamma-quanta can be a signature of the state from which the positron annihilates. As an example, in aluminium the mean positron lifetime in the perfect lattice, in a mono-vacancy, and in a large void is 162, 245, and 500 ps [15,16], respectively. In metals, gases also trap at defects and at particle surfaces, whence the annihilation characteristics of the positron will be affected [1]. This provides the possibility to employ positron annihilation spectroscopy to the study of gas adsorption and desorption processes.

At surfaces, and in some insulators, the positron may also enter a bound positron-electron state, positronium (Ps). para-Ps annihilates by $2\gamma$ annihilation, while intrinsic annihilation of ortho-Ps results in the emission of three $\gamma$-quanta. The intrinsic lifetime of o-Ps is 140 ns, substantially longer than for other positron states, but the lifetime of o-Ps may be strongly reduced by annihilation of the positron with surrounding electrons (pick-off annihilation), which results in the emission of two $\gamma$-quanta. The long lifetime of o-Ps and the wide energy distribution of $3\gamma$ annihilation quanta allows for a relatively easy detection of o-Ps.