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Characterization of lattice defects in metallic materials by positron annihilation spectroscopy: A review

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ABSTRACT

Positron is an excellent probe of lattice defects in solids. A thermallized positron delocalized in lattice can be trapped at open volume defects, e.g. vacancies, dislocations, grain boundaries etc. Positron annihilation spectroscopy is a non-destructive technique which enables characterization of open volume lattice defects in solids on the atomic scale. Positron lifetime and Doppler broadening of annihilation photo-peak are the most common observables related to positron annihilation process. Positron lifetime spectroscopy enables to identify defects in solids and to determine their concentrations while coincidence measurement of Doppler broadening provides information about local chemical environment of defects. This article provides a review of the state-of-art of defect characterization in bulk metallic materials by positron annihilation spectroscopy. Advanced analysis of positron annihilation data and recent developments of positron annihilation methodology are described and discussed on examples of defect studies of metallic materials. Future development in the field is proposed as well.

1. Introduction

Open volume defects of crystallite lattice, e.g. vacancies, dislocations, grain boundaries etc., have a strong influence on many physical properties of metallic materials. For example vacancies play the key role in diffusion processes [1] and phase transformations [2]. Dislocations and grain boundaries cause strengthening of materials [3,4] and provide nucleation sites for precipitation. There is a variety of methods for introducing various lattice defects into metallic materials, e.g. quenching, severe plastic deformation, hydrogen loading, electron and ion irradiation etc. Recently, a number of novel metallic materials with unique physical properties have been developed by a controlled introduction of specific lattice defects. This approach can be called as defect engineering, i.e. tailoring of material properties by a controlled introduction of various lattice defects. Several examples of defect engineering can be mentioned:

(i) The development of a broad class of ultrafine grained (UFG) materials by severe plastic deformation [5–7], i.e. structure refinement by severe plastic deformation introducing a high density of dislocations and a huge concentration of vacancies.
(ii) The design of hardenable Al-Si-Mg based (6xxx series) alloys by micro-alloying with elements having a high binding energy with vacancies [8–10]. This way one can control natural ageing of Al-Si-Mg alloys and also the strengthening effect during subsequent artificial ageing.
(iii) The enhancement of the equilibrium concentration of vacancies by hydrogen loading. The formation energy of open volume defects can be significantly lowered by absorbed hydrogen. This effect is responsible for creation of so-called superabundant vacancies in various metals [11–14]. Hydrogen-induced defects represent just a special case of more general phenomenon explained by the theory of 'defactants = DEFect ACTing AgeNTS' [15,16]. This phenomenon enabling manipulation of the concentration of open volume defects by varying the concentration of defactants opened new space for defect engineering in metallic materials.

Defect engineering approach requires a precise characterization of lattice defects in materials studied. This is challenging task, which requires atomic scale resolution and very high sensitivity to defects, since even low concentration of defects may have a significant influence on the material properties. For example that the concentration quenched-in vacancies in solution treated Al-Si-Mg alloys does not exceed 10^{-4} at.$^{-1}$ [17] but they govern the magnitude and kinetic of the strengthening of these alloys during

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storage at ambient temperature. This is demonstrated by the fact that natural ageing of these alloys can be inhibited by trapping of the quenched-in vacancies by suitable solutes (e.g. Sn) [8,9]. Similarly the concentration of neutron irradiation induced vacancies in the steel of reactor pressure vessel in nuclear power plants is in the order 10^{-4} at.$^{-1}$ [18]. Despite their relatively low concentration the irradiation-induced vacancies are responsible for solute clustering during long-term irradiation leading finally to embrittlement of the steel demonstrated by an increase in the ductile-to-brittle transition temperature that marks the transition between low toughness brittle (cleavage) and high toughness ductile (microvoid coalescence) fracture regimes [19,20].

Positron annihilation spectroscopy (PAS) [21,22] represents an excellent tool for characterization of lattice defects: (i) PAS exhibits a high sensitivity to open volume defects; (ii) the positron as point-like particle acts as highly mobile probe enabling to study material structure on the atomic scale; (iii) PAS is a non-local technique providing information averaged from a macroscopic volume; (iv) PAS is a non-destructive method allowing repeated measurement of samples in order to monitor development of defects during various treatments e.g. annealing, deformation, hydrogen loading, irradiation etc. Theory of positron annihilation in solids [23] is well developed in particular for metals. Positron observables can be calculated from the first principles and directly compared with experiment.

There are several excellent reviews [24–29] describing PAS studies of defects in solids. Early *in situ* studies of equilibrium concentrations of vacancies in metals were reviewed by Seeger [24]. PAS investigations of phase transitions and precipitation effects in age-hardenable systems (mainly Al alloys) were summarized by Dupasquier et al. [25] and Somoza et al. [26]. The review by Tuomisto and Makkonen [27] is focused on the characterization of defects in semiconductors by PAS techniques. Surface studies by slow positron beams were reviewed by Schultz and Lynn [28] and recently by Hugenschmidt [29]. The aim of the present review is description of the recent progress in PAS characterization of lattice defects in bulk metallic materials. The present review is focused mainly on the recent developments in the analysis of PAS data and on the interpretation of PAS data with aid of *ab-initio* calculations. The paper is organized as follows: brief description of the PAS methodology is given in Section 2. The Section 3 describes PAS investigations of various kinds of open volume defects, namely vacancy-like defects, dislocations, grain boundaries and precipitates. Future development in the field is proposed in Section 4. The paper is summarized in Section 5.

2. Positron annihilation spectroscopy

PAS offers a number of various experimental techniques each suitable for characterization of different properties of materials. PAS techniques include (i) positron lifetime (LT) spectroscopy [21,22] which enables identification of open volume defects and determination of their concentration; (ii) coincidence Doppler broadening (CDB) spectroscopy [30,31] which provides information about local chemical environment of defects; (iii) angular correlation of annihilation radiation (ACAR) [32,33] which is suitable for investigation of the electronic structure of materials; (iv) variable energy slow positron annihilation spectroscopy (VEPAS) [28,29,34] which enables determination of the defect depth profile and measurement of the positron diffusion length; (v) age momentum correlation (AMOC) [35,36] which allows study of free volumes in polymers and porous materials and also chemical reactions involving positrons and positronium. Since the present paper is focused on PAS studies of bulk metals we restrict ourselves to LT and CDB spectroscopy representing the most important methods for defect characterization in metallic materials.

2.1. Positron sources

$^{\beta+}$ radioisotopes are used most frequently for generation of positrons for PAS studies. Positrons are emitted by the decay process

$$p^+ \rightarrow n^0 + e^+ + \nu_e, \tag{1}$$

where p^+ and n^0 denotes proton and neutron, respectively, ν_e is the electron neutrino and e^+ denotes positron. Among β^+ radioisotopes ^{22}Na (half lifetime of 2.6 years) is most commonly used for PAS studies. It decays to ^{22}Ne and the daughter nucleus de-excites by emission of a γ ray with energy of 1274 keV, so-called start signal. Since the lifetime of the excited state of ^{22}Ne is a few ps only the γ ray is emitted practically simultaneously with positron and provides, thereby, important information at what time the positron was born.

Conventional β^+ radioisotope positron sources are prepared usually by sealing a small drop of ^{22}Na activity (typically $\sim$1 MBq) between two thin metal or polymer foils [37]. This source is sandwiched between two pieces of the studied sample to ensure that a positron emitted in any direction penetrates into the sample. As a consequence there is always some fraction (usually a few percentages) of positrons annihilating in the positron source spot and the covering foil. This so-called source contribution has to be determined using suitable reference sample and subtracted from PAS spectra [38–41].

Besides conventional radioisotope positron sources there are also intensive positron sources based on generation of positrons by pair production. High energy γ rays necessary for this process are obtained either from bremsstrahlung of electrons accelerated by LINAC [42–44] or from capture of thermal neutrons produced by a nuclear reactor in Cd target [29,45–47].

2.2. Positron annihilation in solids

Positrons emitted by a ^{22}Na radioisotope have continuous spectrum of energies with the end-point-energy of E_{max} = 0.545 MeV. When a positron penetrates into a solid it loses its kinetic energy by ionization, excitation of electrons [48–52] and scattering at phonons [53,54] till its energy decreased down to the thermal energy 3/2 kT, i.e. $\approx$0.04 eV at room temperature. This process is called thermalization and in metallic materials it takes a few ps only. The positron implantation profile is described by the exponential probability density function [55]

$$P(z) = \alpha e^{-\alpha z}, \tag{2}$$

where z is the depth from the sample surface and the parameter α is given by the expression

$$\alpha \left[\mathrm{cm}^{-1}\right] = 16 \frac{\rho \left[\mathrm{g\ cm}^{-3}\right]}{E_{max}^{1.4}\,[\mathrm{MeV}]}. \tag{3}$$

The symbol ρ in the latter expression denotes the density of the sample. The mean positron penetration depth is $1/\alpha$. Using Eq. (3) one can easily calculate that the mean positron penetration depth in metals falls into the range 10–160 μm.

Positron in a solid is finally annihilated by one of surrounding electrons and the annihilating electron-positron pair is converted in the most cases into two annihilation γ rays as shown schematically in Fig. 1. In the centre-of-mass frame the annihilation γ rays fly in strictly opposite directions and their energy is exactly m_0c^2 = 511 keV each. Note that m_0 is the rest mass of electron and c is the speed of light. Non-zero momentum $\boldsymbol{p}$ of the annihilating pair

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