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Investigation of the dependence of phosphorus segregation on grain boundary structure in Fe-P-C alloy: cross comparison between Atom Probe Tomography and Auger Electron Spectroscopy

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ABSTRACT

Intergranular segregation in a Fe-P-C model alloy after thermal ageing at 650°C has been examined using Atom Probe Tomography (APT) and Auger Electron Spectroscopy (AES). The specimens were prepared using site-specific method combining focused ion beam (FIB) and Transmission Kikuchi Diffraction (TKD). Grain boundary's five macroscopic degrees of freedom (DOFs) were determined from the TKD map supplemented by 3D APT reconstruction. The phosphorus intergranular segregation values obtained using APT and AES techniques were in excellent agreement and equal to 1.6 ± 0.7 at/nm^2 and 1.4 ± 0.5 at/nm^2, respectively. The two techniques are complementary for a fully quantitative description.

1. Introduction

The intergranular segregation of phosphorus in steel can diminish the cohesion between the grains and raise the ductile-to-brittle transition temperature (DBTT). For this reason, the effect of phosphorus on the embrittlement of steel has been intensively studied over the past few decades. Most of the experimental studies were carried using Auger Electron Spectroscopy (AES). Measurement of phosphorus and carbon intergranular segregation in Fe-P and Fe-P-C model alloys has been reported by Erhart and Grabke [1]. It was shown that the intergranular segregation of phosphorus increases with increasing the bulk concentration of phosphorus and decreasing the temperature of annealing. All the data could be evaluated using the Langmuir-McLean [2] equation for equilibrium segregation. With increasing the carbon bulk concentration, the intergranular segregation of phosphorus decreases, which can be explained in terms of site competition between phosphorous and carbon atoms at the grain boundary (GB) [1,3,4] or as a consequence of repulsive chemical interaction between these two species [5,6]. Since it is not easy to distinguish between repulsive interaction and site competition of phosphorus and carbon atoms [7] it was assumed that both of them can contribute to the final value of segregation.

Many AES investigators reported a wide scatter (up to ± 40 rel.%) of intergranular phosphorus segregation in α-iron and ferrite-based steels, which is most probably associated with the variation of the GB structure in the polycrystal [8–13]. Later, more detailed studies on relationship between the GB structure and intergranular segregation were done using bicrystals with particular well-defined GB geometries [6,14–18]. Based on a systematic experimental study, Lejček et al. [19–21] have provided an extension of the model of Seah and Hondros by considering the GB structure and non-ideal behavior of the solid solution at the solubility limit. The model allows to predict the variation of standard segregation enthalpy, ΔH^0, with the GB orientation (special, general and vicinal GBs), annealing temperature and the bulk solid solubility. However, some questions, such as, the distribution of segregating elements in structurally different GBs, including twist, asymmetrical and mixed ones; the effect of the GB plane; the faceting and the segregation dependent structural changes are still open and require additional theoretical and experimental studies.

In order to improve the understanding of segregation phenomena, it is necessary to know the arrangement of segregated solutes at the atomic scale and the dependence of the GB composition from the GB crystallography. In the present work, the local GB composition was measured by Atom Probe Tomography (APT) and the GB crystallographic parameters were determined by combination of Transmission Kikuchi Diffraction (TKD) mapping and 3D Atom Probe reconstruction.

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Both APT and AES techniques have own advantages. In comparison with AES, APT provides more accurate measurement of the GB chemistry and in combination with TKD gives complete information about the structure of GB in the polycrystal. However, it is worth acknowledging that AES is a cheaper and faster method, and is widely used. Thus, the combination of APT and AES techniques can simultaneously improve the accuracy and the statistics of GB segregation measurements.

The aim of the work presented here is to develop an experimental atomic-scale methodology to study the phosphorus intergranular segregation as a function of GBs parameters, apply it here to Fe-P-C model alloy after thermal heat treatment and to compare results with AES measurements. Moreover, although until now both APT and AES have been widely used to study GB segregation, there are only very few works comparing them [22].

2. Material and methods

The material studied in this work is a high purity Fe-0.034 at.% P-0.01 at.% C model alloy. The ingot of 110 × 110 × 80 mm^3, supplied by OCAS (Belgium), was cast in a vacuum induction furnace. After reheating at 1200 °C, it was hot rolled in six passes down to 20 mm in thickness. Then it was air-cooled down to the room temperature. Sample of size of 20 × 20 × 20 mm^3 was prepared and held at 650 °C for 2 h and then air cooled to room temperature. The annealing at 650 °C during 2 h simulates the post weld heat treatment of Reactor Pressure Vessel (RPV) steel in the industry. To ensure that the equilibrium value of phosphorus intergranular segregation is reached, a heat treatment in the same conditions but during 24 h was also done on additional samples of 4 × 20 × 2 mm^3 size.

Specimens in the form of plates of 4 × 4 × 2 mm^3 were cut and polished with abrasive paper down to 4000 grit, followed by polishing using a diamond paste of 3 µm and 1 µm size. In the final step, the samples were polished using an aluminum oxide polishing paste of 0.1 µm grit size and cleaned in ethanol in an ultrasonic cleaner.

Electron backscattered diffraction (EBSD), TKD mappings and the site-specific preparation of atom probe samples were performed in a Zeiss NVision 40 dual-beam Focus Ion Beam Scanning Electron Microscope (FIB-SEM) equipped with an HKL Nordlys S camera. Data acquisition was managed with the Oxford Instruments AZtec. First, a GB for site-specific preparation is selected from the EBSD orientation map. In order to visualize the EBSD orientation data, the inverse pole figure (IPF) mapping was used. For each map, a reference sample direction is selected (X, Y or Z) and the color assignment is done. Then, a small chunk (2 × 2 × 10 $µm^3$) containing the selected GB is cut from the sample and lifted-out thanks to the micromanipulator. The position of the GB in the APT needle has to be nearly perpendicular to the tip axis to minimise the local magnification effect [23]. Finally, annular milling is performed to form the APT sample with a radius of curvature of about 10 nm. The milling process is controlled thanks to TKD. The idea is to make the TKD orientation map and identify the GB position after each annular milling step [24]. Several repetitions of FIB annular milling with consequent TKD mapping are required to place the GB close (< 50 nm) to the tip apex. Final milling is performed at 2 kV to "clean" the sample from Ga^+ ions.

A local-electrode atom probe (LEAP) 4000 HR from Cameca was employed to measure the GB composition. The atom probe analyses were performed in voltage mode. The pulse fraction and the pulse repetition rate were 20% and 200 kHz, respectively. To remove the surface oxides, the initial evaporation temperature was around 80 K, and then cooled down to 50 K. To ensure that the experimental conditions provide reliable composition, calibration experiments were performed with pulse fractions equal to 15% and 20% of the standing voltage, with a range of specimen temperature from 20 K to 80 K. No influence of pulse fraction and temperature was observed at temperatures below 60 K. The temperature of analysis was thus fixed to 50 K to get reliable composition and limit the risk of fracture of the samples during the analysis. Data reconstruction was performed using IVAS 3.6.0 (Cameca Instrument). All further steps of data mining were done with the GPM 3D soft 6.0 developed at the laboratory GPM, University of Rouen Normandy. The reconstruction parameters were calibrated to obtain the correct interplanar spacing in the analysis direction and good angles between poles on desorption figure.

AES experiments were performed with a Thermo VG ThetaProbe spectrometer, using a field emission gun operating at 10 kV accelerating voltage and a 3 nA beam current. The angle of incidence of the electron beam was 45° with respect to the specimen surface resulting in a spot size of approximately 150 nm. Spectra were acquired on a hemispherical analyser in the fixed retard ratio mode. Two specimens with the same heat-treatment (2 h at 650 °C) were studied. Samples were prepared as parallelepipeds of approximately 2 × 2 × 15 mm^3, with a notch at the midpoint. Each AES specimen was introduced into the preparation chamber of the spectrometer (~5 × 10^{-8} Pa) and cooled down to −90 °C. The specimen was then fractured by impact bending and one half of the broken specimen was transferred into the analysis chamber (~2 × 10^{-7} Pa). Analyses were performed in spot mode, where spots were located by the operator in intergranular areas of the fracture surface. For each analysis spot, an AES spectrum was acquired in the energy range 0–800 eV.

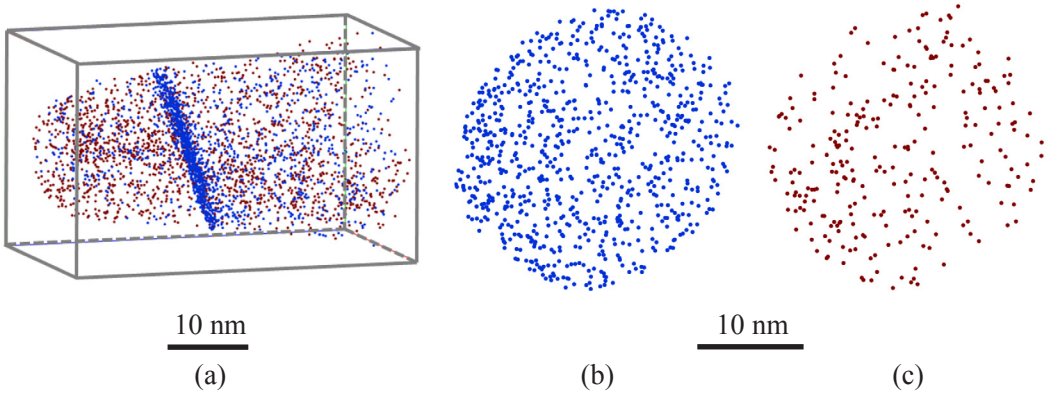

Fig. 1. APT reconstruction of a small volume of the Fe-0.034 at.% P-0.01 at.% C model alloy after annealing at 650°C during 24 h showing (a) the segregation of phosphorus (blue) and carbon (red) atoms at a HAGB and homogenous distribution of (b) phosphorus and (c) carbon atoms on the GB plane. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)