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# Study by EELS of helium bubbles in a martensitic steel

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ABSTRACT

This work presents measurements of the helium density and pressure in small bubbles in a martensitic steel, which is a vital first step towards identifying their role in the microstructural mechanisms determining the macroscopic properties of the material. Electron Energy-Loss Spectroscopy in the Scanning Transmission Electron Microscope has been used to analyse individual bubbles. The energy shift of the 1s → 2p transition and the helium density have been measured for each bubble analysed. The pressure inside the bubbles has been calculated from the helium density using an equation of state. In these bubbles, the values for the helium pressure seem to be smaller than the equilibrium pressure, and agree in trend with the findings of previous studies, although our results extend to smaller radii and higher pressures.



## 1. Introduction

This paper presents a study of homogeneously α-implanted specimens of a 9Cr–1Mo (EM10) martensitic steel at 550 °C to a concentration of 5000 appm. At this implantation temperature, He bubbles are easily observed by conventional TEM. The bubble number density and size had been previously determined [3,4]. However the He density itself is not attainable by conventional TEM. This is the motivation for the study of He bubbles by Electron Energy-Loss Spectroscopy (EELS).

Such bubbles can be produced under certain irradiation conditions in metallic materials due to the extremely low He solubility. The bubbles can cause a significant loss of ductility. This subject is of concern for the steels to be used in the future for fusion applications; embrittlement by helium is regarded as one of the effects which could limit the lifetime of structural materials in this context. Many investigations have already been conducted to identify the effect of He bubbles on metal mechanical properties. The initial studies [5–7] aimed at understanding the mechanism of He bubble formation. The influence of implantation conditions on bubble size distributions [8] and the effect of implanted He on the mechanical properties [9] have been studied and it has been shown that helium can induce a severe loss of ductility [3,4]. Thus, it is important to understand the mechanisms involved in formation and growth of the bubbles.

Knowledge of the He density existing in these small bubbles is prerequisite for this. Recent experimental studies [2,10] have shown that Scanning Transmission Electron Microscopy combined with Electron Energy-Loss Spectroscopy (STEM–EELS) is a powerful technique for He bubble analysis. It can be used to calculate the He density in individual bubbles.

The aim of this work is to obtain the helium density and pressure in very small bubbles. The He density is directly measured from the electron energy-loss signal, using a method developed by Walsh et al. [2]. Then, the appropriate equation of state [1] can be used to calculate the pressure in the bubbles from the He density.

## 2. Experimental procedure

### 2.1. Microstructural observations

He bubbles were first examined by Transmission Electron Microscopy (TEM). Following implantation and testing of tensile specimens, a 2 mm diameter disc was punched from the gauge section of each specimen and thin foils suitable for TEM examinations were prepared by jet-electropolishing. A JEOL 2000 EX and a TEM TECNAI F20 were used for standard observations (images and diffraction). In order to observe the He bubbles, a negative defocus was used, generating Fresnel fringe contrast around the bubbles. Energy-loss analyses were performed in a VG HB501 STEM operat-

*Abbreviations:* EELS, Electron Energy-Loss Spectroscopy; STEM, Scanning Transmission Electron Microscope.

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ing at 100 kV, and equipped with a GATAN 666 spectrometer. Details of this technique are presented in Section 3.

*2.2. Material*

The material investigated in this study is a martensitic steel (EM10 grade). The nominal chemical composition is given in Table 1.

Plates with an initial thickness of 0.5 mm were cold-rolled to a final thickness of about 100 μm. After rolling, heat treatments were carried out. The following normalisation and tempering conditions were applied: 1 h at 1050 °C plus 1 h at 760 °C. The resulting microstructure of the steel consisted of 200-300 nm wide martensite laths in the prior-austenite grains of average size 21 μm. The specimens were implanted with 5000 appm He at 550 °C. The irradiation apparatus is located at a beam line of the Jülich Compact Cyclotron. The initial energy of the α-beam (27.4 MeV) was then degraded by a rotating wheel consisting of 24 aluminium foils of different thicknesses. In order to obtain a homogeneous implantation, the beam was scanned at sawtooth frequencies of typically 300 Hz in both directions across the specimen. More details of the He implantation process are given by Henry et al. [4]. Before TEM characterisation, the implanted specimens were mechanically tested at room temperature. The results of these tensile tests are presented in Ref. [4]. Tensile tests performed on EM10 samples implanted to 0.5 at.% He at 550 °C indicated helium-induced hardening. However, significant ductility was retained at this implantation temperature. After He implantation and mechanical characterisation, the microstructure (Fig. 1) shows He bubbles nucleated at dislocations, lath and sub-boundaries and precipitates.

The bubbles are small (average diameter 5–10 nm) and clearly facetted (Fig. 2). Fig. 2(a) and (b) shows TEM images along ⟨1 1 1⟩ and ⟨1 1 3⟩ directions respectively. The bubbles appear for the most part as hexagons in the ⟨1 1 1⟩ direction (Fig. 2(a)) and as somewhat irregular rectangles or parallelograms in the ⟨1 1 3⟩ direction (Fig. 2(b)). The bubbles are thus most likely to be cuboids in which the facets are parallel to the (1 0 0) planes. This feature is

**Table 1**
Chemical composition of EM10 (in wt%).

| Steel | C | Cr | Mo | V | Nb | Ni | Mn | N | P | Si |
|---|---|---|---|---|---|---|---|---|---|---|
| EM10 | 0.1 | 8.8 | 1.09 | – | – | 0.18 | 0.51 | 0.02 | 0.02 | 0.37 |

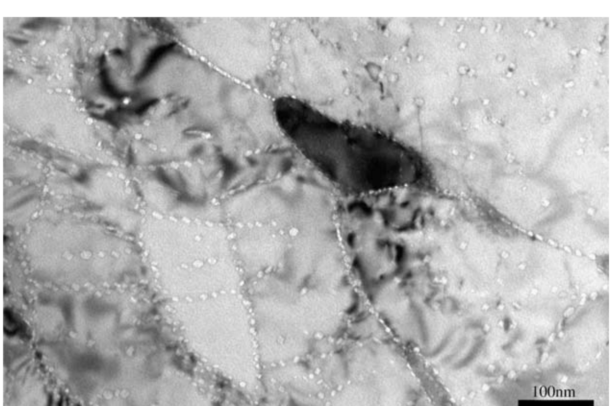


**Fig. 1.** TEM micrograph of typical He bubble microstructure in EM10 post implantation.

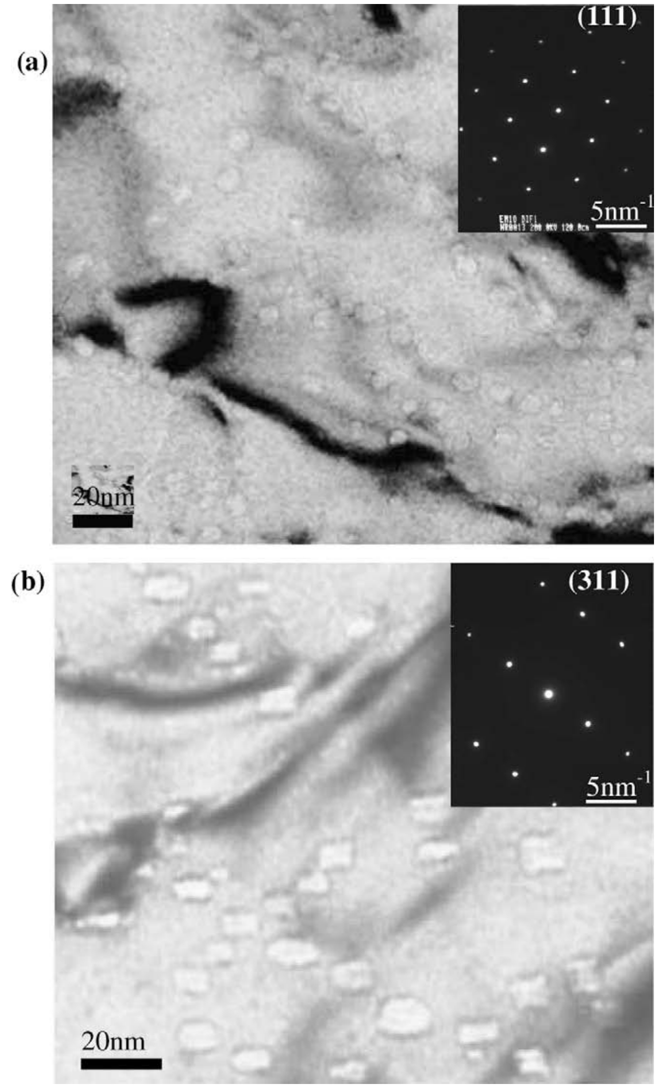


**Fig. 2.** (a) TEM bright field micrograph obtained along the [1 1 1] zone axis and the corresponding diffraction pattern and (b) TEM bf micrograph obtained along the [3 1 1] zone axis and the corresponding diffraction pattern.

consistent with the results of the literature [11,12]. In bcc metals, the {1 0 0} surface energy is significantly reduced compared with other orientations. Some bubbles are elongated. This elongation is not due to the stress created during the tensile tests; such microstructure has also been observed in unstressed implanted specimens.

## 3. Method of analysis

EELS experiments have been used before to measure the He density in bubbles [13–16]. The main result of these studies was that the energy of the 1s–2p transition, which is at 21.218 eV [18] for the dilute gas (or for the He free atom) is shifted towards higher energy in the bubbles. The peak position has also been measured by ultraviolet absorption. A linear relationship between the energy shift ($\Delta E$) and the He density $n$ is obtained:

$$\Delta E = Cn. \quad (1)$$

The energy shift can thus be used to determine the He density by calculating the proportionality coefficient $C$. Lucas [14] obtained