RAPID COMMUNICATION

# Atomic origins of solid helium bubbles in tungsten*

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Solid helium bubbles were directly observed in the helium ion implanted tungsten (W), by different transmission electron microscopy (TEM) techniques at room temperature. The diameters of these solid helium bubbles range from 1 nm to 8 nm in diameter with the mean bubble size about 3 nm. The selected area electron diffraction (SAED) and fast Fourier transform (FFT) images revealed that solid helium bubbles possess body-centered cubic (bcc) structure with a lattice constant of 0.447 nm. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images further confirmed the existence of helium bubble in tungsten. The present findings provide an atomic level view of the microstructure evolution of helium in the materials, and revealed the existence of solid helium bubbles in materials.

**Keywords:** solid helium bubble, atomic origins, tungsten, TEM, HAADF-STEM

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## 1. Introduction

It is well known that helium can introduce serious degradation effects on the mechanical properties of various metals and alloys.[1,2] The behavior of helium in materials has been studied extensively for several decades in the nuclear materials community, particularly in relation to fusion reactors. Although helium bubbles have been widely observed in neutron or ion irradiated materials, the atomic information of helium inside bubbles is still little known. Some studies predicted that helium could be in solid phase inside bubbles by either modeling or helium pressure analysis.[3–6] However, so far there is still no direct evidence showing solid structure of helium bubbles. In this work, different electron microscopy techniques were carried out to reveal solid helium bubbles in helium-implanted W, and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images further confirmed the existence of helium bubble in tungsten.

## 2. Methods

TEM lamellae with a size of about $3 \times 10$ μm, and thickness $< 50$ nm were prepared by using the focused ion beam (FIB) technique from pure W. The TEM lamellae was implanted with helium ions of energy 15 keV at about 873 K. The helium ion beam had a flux of about $3.5 \times 10^{16}$ He+/m$^2$/s. The samples were implanted to about $1 \times 10^{21}$ He+/m$^2$ in 8 hours. The projected range of the helium ion in W was about 100 nm, calculated with the stopping and range of ions in matter program (the SRIM code). The average helium concentration was about 15 at.%. TEM observation was performed using JEOL 2010, and FEI Tecnai F20 microscopes, all operated at 200 kV.

## 3. Results and discussion

Helium bubbles were detected by employing the Fresnel imaging technique in under- and over-focus conditions. Figure 1 is a pair of TEM micrographs taken in the same area showing a view of helium bubbles (a) in under-focus ($-258$ nm) imaging condition and (b) in over-focus (+258 nm) imaging condition. In Fig. 1(a) dark fringes appear as surrounding light dots; while in Fig. 1(b) light fringes appear surrounding dark dots. These are typical images of bubbles or cavities. The size of bubbles ranges from 1 nm to 8 nm in diameter with the mean bubble size about 3 nm.

Stereo-pair imaging technique is further applied to determine the distribution of bubbles and to confirm that these features are not surface artifacts induced by specimen prepara-

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tion or other precipitates. To obtain a stereo-pair images, two identical images have to be taken at two orientations with a difference of 10°–15°. Figure 2 presents a stereo pair of micrographs taken from the same area of Fig. 1 with a difference of 14° in tilting angle. One can clearly see that the helium bubbles are uniformly distributed in the specimen.

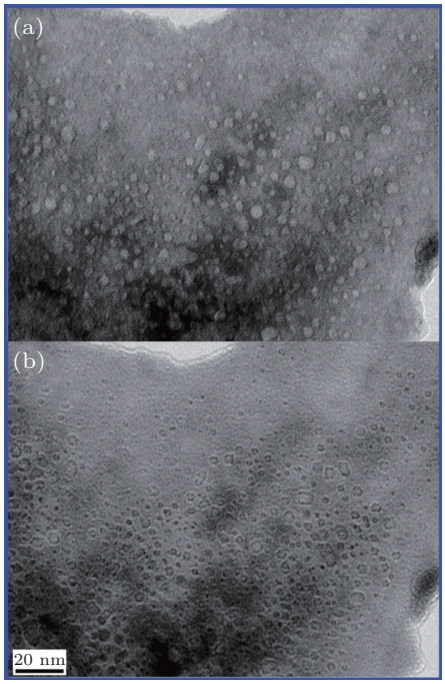



**Fig. 1.** (color online) TEM images of helium implanted W: (a) in under-focus (−258 nm) and (b) in over-focus (+258 nm) imaging conditions.

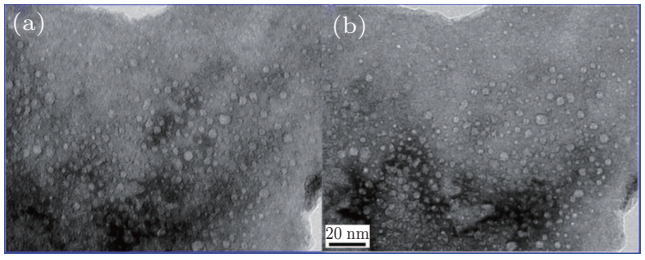



**Fig. 2.** (color online) Stereo pair images of helium implanted tungsten taken in two different zone axis directions with a difference of 14°.

The solid crystalline helium bubbles were detected from the diffraction patterns of the sample. As shown in Fig. 3(a), besides the bright diffraction spots of W, there is another set of spots with weaker intensity. Figure 3(b) is a typical dark field image taken from a weaker diffraction spot. It demonstrates a crystalline structure of the bubbles. The bubbles are slightly elongated and blurred due to image drift occurring during the long exposure time.

The intrinsic structure of individual helium bubbles and the orientation relationship between the helium bubbles and the W matrix were further investigated in detail by using high resolution transmission electron microscopy (HRTEM). More than twenty helium bubbles were analyzed.

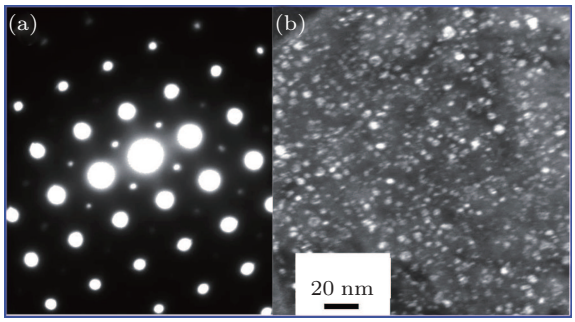



**Fig. 3.** (color online) (a) A diffraction pattern taken from the helium implanted W sample showing the superposition of the diffraction patterns of tungsten and helium; (b) a dark field image taken from a helium diffraction spot.

Figures 4 and 5 show HRTEM images of helium bubbles (about 4 nm in diameters) in two different zone axis directions. As can be seen in Fig. 4(a), the lattice spacing distance of the bubble is obviously different from that of W matrix. Figure 4(b) is the fast Fourier transform (FFT) image of the marked square region 1 in Fig. 4(a). It also reveals a single-crystalline feature with bcc structure in zone axis $[1\bar{1}\bar{2}]$ surrounded by W matrix in zone axis $[\bar{2}20]$. The $d$ spacing of (110) plane of bubble measured from the Fourier filtered HRTEM image in Fig. 4(c) is 0.316 nm, and the deduced lattice constant is 0.447 nm, which is exactly same as that obtained from diffraction pattern in Fig. 3(a). Figure 4(d) is the FFT image of the W matrix corresponding to the region 2 in Fig. 4(a). It shows that the W matrix possesses a bcc structure (lattice constant $a$ 0.316 nm), and the $d$ spacing 0.158 nm measured directly from the W matrix refers the (002) plane. An orientation relationship between the helium bubble and the W matrix derived from the FFT image is: $(110)_{\mathrm{He}} \parallel (002)_{\mathrm{W}}$ and $[1\bar{1}\bar{2}]_{\mathrm{He}} \parallel [\bar{2}20]_{\mathrm{W}}$. Figure 5 presents an image in another zone axis direction. The bubble in region 1 shows a very clear cubic crystalline structure. Figure 5(b) is the FFT image of the marked square region 1, which reveals a pattern being the same as the diffraction pattern in Fig. 3(a). The corresponding $d$ spacing of (110) plane measured from the image of the bubble is 0.316 nm, which gives a lattice constant $a$ 0.447 nm, too. Similarly, the $d$ spacing of (002) plane measured from region 2 is 0.158 nm, which is consistent with the value measured from Fig. 4. The orientation relationship between the He bubble and the W matrix in Fig. 5 is: $(110)_{\mathrm{He}} \parallel (002)_{\mathrm{W}}$ and $[00\bar{2}]_{\mathrm{He}} \parallel [0\bar{2}0]_{\mathrm{W}}$. The results of conventional TEM and HRTEM observations are in perfect agreement. We are fully convinced that helium bubbles, at least those with sizes below about 4 nm, possess bcc crystalline structure with a lattice constant of 0.447 nm in the present experimental conditions.

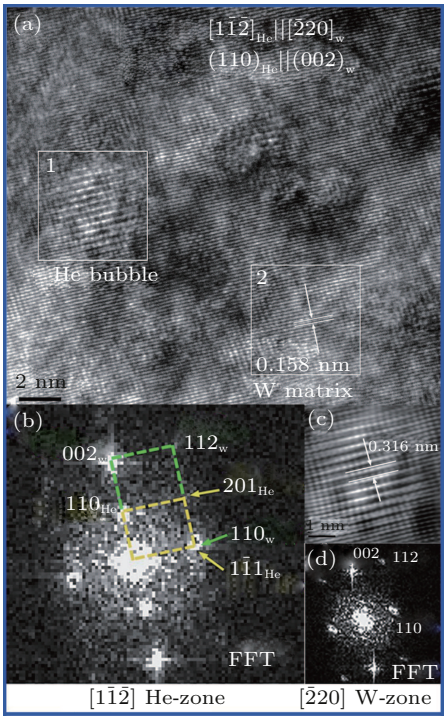



**Fig. 4.** (color online) (a) HRTEM image of helium bubbles in the tungsten matrix; (b) FFT image of the helium bubble in region 1; (c) the Fourie filtered HRTEM image taken from region 1; and (d) FFT image of the tungsten matrix in region 2.

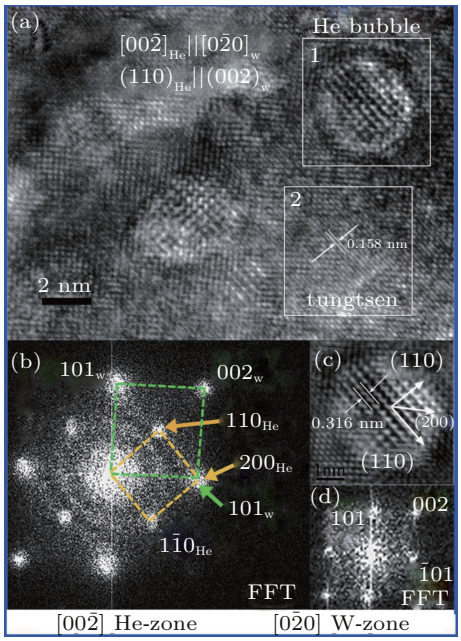



**Fig. 5.** (color online) (a) HRTEM image of helium bubbles in another area and zone axis direction; (b) corresponding FFT image of region 1; (c) Fourie filtered HRTEM image taken from region 1; and (d) FFT image of the tungsten matrix in region 2.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) is currently widely used as an analytical tool that can provide "chemical" information at atomic resolution, since the HAADF-STEM image intensities correspond directly to the atomic number ($Z$) of constituent atoms in the materials. Figure 6 shows the HAADF-STEM images of the typical solid helium region. The strong intensity in the HAADF image is observed in this region as shown in Figs. 6(a) and 6(b), the bright area was definitely known as W, since W possess high $Z$ number ($Z = 74$). On the other hand, the dark spots indicate the existence of low $Z$ number elements or the surface roughness-induced image intensity. As shown in Figs. 6(a) and 6(b), dark spots were uniformly distributed in W, the diameter of the dark spots was about 3 nm–5 nm, and the dark spots were circular or nearly circular, which were consistent well with the solid helium bubbles observed in TEM images. This indicates that dark spots in HAADF image are helium bubbles.

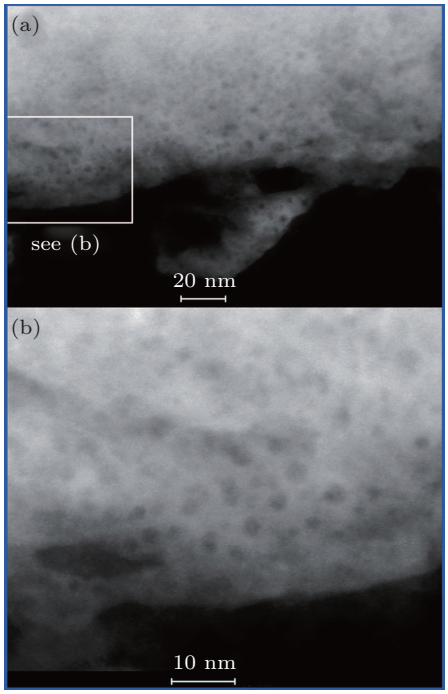



**Fig. 6.** (color online) (a) HAADF-STEM image of the typical region of helium-implanted W; (b) Magnified image in the square region in panel (a).

As shown in Figs. 4 and 5, different zone axis HRTEM images show the same results, that are $(110)_{He} \parallel (002)_{W}$, and the $d$ spacing of He (110) plane (0.316 nm), correspond well with the W lattice constant $a$ 0.316 nm ($d$ spacing of (001)w). These results suggest that He atoms push out W atoms and stay in the positions of W atoms means lattice sites, so then the W atoms become interstitial atoms and they bond with each other to form dumbbell in the direction of $\langle 100 \rangle$. Obviously, TEM and HADDF-STEM results both indicate the existence of bcc structured solid helium bubbles in W under certain conditions, which is helpful to understand the microstructure evolution of helium in tungsten or other metals.

As mentioned earlier, some studies predicted that helium could be in solid phase inside bubbles by either modeling or

helium pressure analysis.[3–6] Among these studies, some also performed TEM and HRTEM observations.[3,5] But, none of them could show a diffraction pattern to domenstrate the bubbles being solid and gave any information about structure and lattice parameter of helium insides bubbles. The extensive phase diagram studies of solid helium employed high pressure compression techniques and demonstrated that solid helium may possess hcp, fcc, bcc structures.[7–9] Schuch *et al.* showed that the helium compressed under high pressure at about 1 K could possess bcc structure,[5] but with lattice constant of 0.411 nm.[10,11] In our experiment, helium is also bcc-structured, however, the lattice constant measured from the diffraction pattern and FFT images is 0.447 nm. Although, the discrepancy between the lattice constant values is not fully understood, it could be due to: (i) Schuch's data were measured at 1.73 K, while our data were obtained at room temperature; (ii) Schuch's data were measured from compressed solid helium crystals, while our results were measured from helium-implanted W. Nonetheless, the studies demonstrated the same bcc structure of solid helium.

Generally in neutron and ion studies the levels of helium of interest range from order one appm He up to about $10^4$ appm helium. The helium level in the W sample of this study is much higher than the reality. This does not mean that the formation of solid helium bubbles can be excluded in the fission and fusion reactor materials, at least before the formation mechanisms are understood.

The present findings provide an atomic level view of the microstructure evolution of helium in the materials, and revealed the existence of solid helium bubbles in materials. We believe that the result is helpful to understand the complex behavior of helium atoms in materials, and thus the microstructural evolution and mechanical properties of materials.

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