OUTLOOKS IN EARTH AND PLANETARY MATERIALS

In-situ high-pressure transmission electron microscopy for Earth and materials sciences

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ABSTRACT

Transmission electron microscopy in combination with in situ high-pressure and high-temperature measurements is uniquely able to provide high-resolution data about materials under conditions resembling those in Earth’s interior. By using nanocontainers made of graphitized carbon, it is possible to achieve pressures and temperatures up to at least 40 GPa and 1500 °C, respectively. A wide range of relatively simple minerals have been studied using this approach. Results to date show the influence of crystallographic defects in concentrating and storing carbon within analogs to minerals occurring deep inside Earth.

Keywords: In situ transmission electron microscopy, high-pressure measurements, carbon nanocontainers, carbon nanotubes (CNTs), carbon nanofibers (CNFs), carbon nano-onions (CNOs)

INTRODUCTION

Transmission electron microscopy (TEM) has long been used to study the products of high-pressure experiments at the near-atomic scale. However, in all cases it has been necessary to quench the samples before they could be imaged at high resolution (Mao and Hemley 1998). Diamond-anvil cells (DACs) and multi-anvil presses (MAPs), the instruments currently used for pressure generation, prevent the in situ use of TEM because their substantial sizes preclude the necessary electron transparency. As a consequence, in situ TEM applications for experiments at gigapascal pressure ranges, particularly meaningful to the Earth sciences, have been impossible up to now.

X-ray diffraction and other spectroscopic techniques available for in situ high-pressure research acquire statistical information averaged over the relatively large sample volumes interacting with the source radiation. However, in many cases, studies of crystal defects and mineral reactions at unit-cell dimensions are central to understanding geophysics and geochemistry in Earth’s interior (Cordier 2002; Karato 2010; Stixrude and Lithgow-Bertelloni 2012). TEM is one of the most useful techniques, and commonly the only one, for observing defect features and analyzing chemical compositions at down to atomic resolutions (Buseck 1992; Veblen 1985). Therefore, in situ TEM capabilities at high pressure have long been desired within the Earth and materials science communities.

The goal of this paper is to provide an overview of recent efforts to develop and refine an in situ, high-pressure TEM method for the Earth and materials sciences. With successful applications to geophysically significant minerals and mineral analogs, we demonstrate the feasibility and potential of this new technique.

GRAPHITIC NANOCONTAINERS AND NANOPRESSES

Graphitic networks can lose carbon atoms through displacement damage and vacancy formation when exposed to electrons with acceleration voltages over ~86 kV in an electron microscope (Smith and Luzzi 2001). If the graphitic networks are curved on the nanometer scale and the temperature is raised to above ~300 °C, structural reorganization occurs around the relatively immobile vacancies in the networks, causing their shrinkage (Fig. 1) (Banhart 1999, 2004; Krasheninnikov et al. 2005). If they are in the form of closed containers that enclose condensed materials, compression of the enclosed materials occurs (Banhart and Ajayan 1996). Calculations indicate that if the containers are sufficiently small, what we call nanocontainers, then the internal pressures can reach 40 GPa in, for example, multi-walled carbon nanotubes (CNTs) (Sun et al. 2006a).

Pressure generation in carbon containers can be understood in terms of Laplace’s law, which relates internal pressure (P) of a fluid-filled hollow vessel to wall tension (T) and its hollow radius (R). For a cylindrical vessel, T = P R, whereas T = P R/2 for a spherical vessel. The wall tension of a 19-shelled CNT is at least 140 N/m (Sun et al. 2006b). Atomistic calculations suggest that internal pressures in multi-walled CNTs converge to a maximum with only ~6 graphitic shells, such that further increases in the number of walls do not produce proportional pressure increases (Sun et al. 2006a). Therefore, for an inner sample diameter of 100 nm, the electron-transparent thickness limit for most materials, maximum internal pressures of greater than 2.8 and 5.6 GPa would be expected in tubular and spherical graphitic containers, respectively.

The workable wall thicknesses are limited by half of the mean absorption distance (λ) for graphite since the container walls both below and above an enclosed sample interact with the incident electrons. For a typical TEM acceleration voltage and collection angle, e.g., 300 kV and 3 mrad, respectively, λ is ~225 nm (Widenkvist et al. 2009).

Carbon nanocontainers enclosing samples of interest can be prepared through either insertion of samples into pre-existing containers or growth around the minerals of interest. If sufficiently thin, the walls of these carbon nanocontainers permit...