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Evidence of amorphisation of B_4C boron carbide under slow, heavy ion irradiation

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ABSTRACT

Boron carbide is widely used either as armor-plate or neutron absorber. In both cases, a good structural stability is required. However, a few studies have shown amorphisation may occur in severe conditions. Hard impacts lead to the formation of amorphous bands. Some irradiations in electronic regime with H or He ions have also shown amorphisation of the material. Most authors however consider the structure is not drastically affected by irradiations in the ballistic regime.

Here, we have irradiated at room temperature dense boron carbide pellets with Au 4 MeV ions, for which most of the damage is in the ballistic regime. This study is part of a program devoted to the behavior of boron carbide under irradiation. Raman observations have been performed after the irradiations together with transmission electron microscopy (TEM). Raman observations show a strong structural damage at moderate fluences (10^{14}/cm^2, about 0.1 dpa), in agreement with previous studies. On the other hand, TEM shows the structure remains crystalline up to 10^{15}/cm^2 then partially amorphises. The amorphisation is heterogeneous, with the formation of nanometric amorphous zones with increasing density. It then appears short range and long range disorder occurs at quite different damage levels. Further experiments are in progress aiming at studying the structural stability of boron carbide and isostructural materials (α-B, B_6Si,...).

1. Introduction

Boron carbide is widely used as neutron absorber in nearly all types of nuclear plants. This choice mainly results from a good availability, a relatively low cost and of course a high neutron absorption efficiency, but certainly not flows from its thermo-mechanical properties, leading to early damage then short life duration. However, it has shown a good structural stability that has been previously insufficiently addressed.

Boron carbide is a light (2.52 g/cm^3 for a 100% dense 'B_4C'), super-hard (Hv ~40 GPa) ceramic [1,2] with a high Hugoniot-limit (HEL~17 GPa) [3]. It has a high stiffness (Young modulus ~450 GPa), high strength (yield ~450 MPa) but a low fracture toughness (K_{IC} ~4 MPa $\sqrt{m}$). This set of properties leads to the first field of applications, as grinding tools, nozzles, armors. Available materials have a composition close to the B_4C formula (cf. infra) but the boron carbide phase exists from about B_4C to about $B_{10}C$ (Fig. 1).

On the other hand, the atomic density is high, the boron content is about 10^{23}/cm^3. Boron is naturally composed of two isotopes, ^{10}B and ^{11}B. 10-boron has a natural concentration of about 20 at.% which industrial processes can modify from less than 1 at.% to more than 99 at.% depending on the applications. ^{10}B has a very high neutron absorption cross section making this element a very efficient neutron absorber in nearly all nuclear reactors (Fig. 2).

^{10}B captures neutrons mainly through the ^{10}B(n,α)^{7}Li reaction: He and Li atoms are produced, with high kinetic energy (He ~1.65 MeV, Li ~0.95 MeV) leading first to high density of atomic displacements. On the other hand, in a fast neutron reactor most neutron interactions are capture-less but can lead to high energy transfers (^{11}B-enriched boron carbide is potentially one of the best neutron moderator), up to about 1 MeV, to the atoms of the material (C, B) here again inducing atomic displacements. In fast neutron reactors, the conjunction of the heat release and of the helium formation leads to a high damage of the material [4]. He (up to 10^{22} at./cm^3 per year) accumulates in flat, highly pressurised, parallel bubbles, inducing local anisotropic swelling and microcracking (Fig. 3). The heat release (up to 100 W/cm^3) induces high radial thermal gradients, then extensive cracking of the

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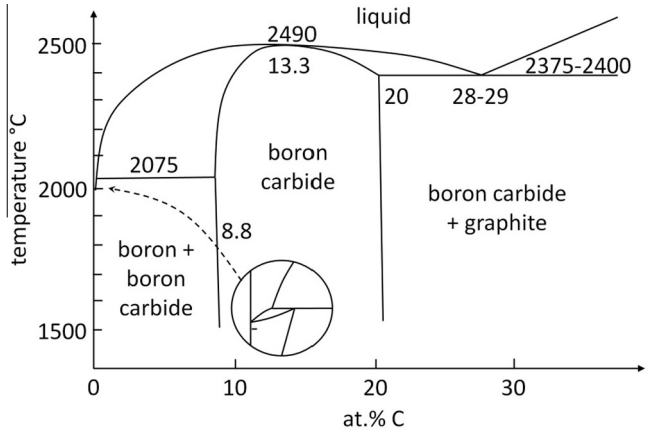

Fig. 1. Boron–carbon phase diagram, from [2]. The carbon-rich limit is presently considered most probably at about 19 carbon at.% [1].

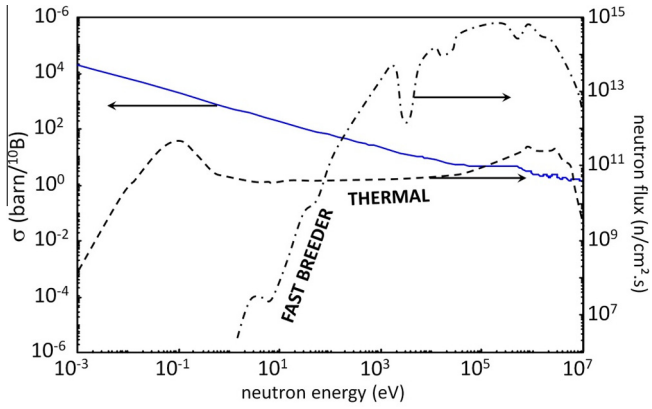

Fig. 2. Neutron absorption cross section for the ^{10}B isotope (full line, from ENDF data base) superimposed to the neutron energy distribution in a PWR (thermal) and a FNR (fast breeder) reactor (from DOE-HDBK-1019/1-93).

absorber pellets. However, it is worth noting post irradiation examinations have shown the material remains crystalline up to the highest boron burnup, that is about 20 at.% total boron.

The details of the crystalline structure of boron carbide has for long been controversial. As an example, the carbon-rich limit of phase has been claimed as $B_{3.8}C$ [5], B_4C (mainly for aesthetics and the sake of simplicity), $B_{4.3}C$ [6]. The structure is rhombohedral, most often described in a hexagonal frame, isostructural to

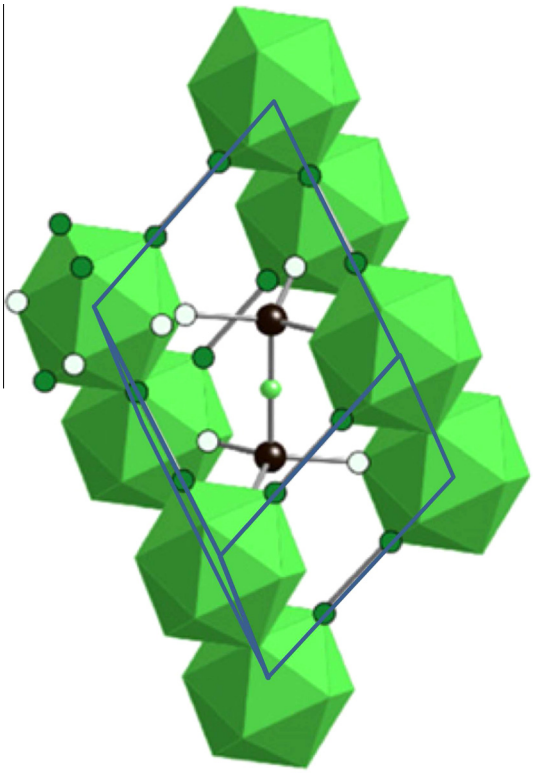

Fig. 4. Cell structure of boron carbide, from H. Werheit et al., J. Phys. Cond. Mat. 24 (2012) 305401.

α-boron and other compounds such as B_6O, or B_6Si. It is built with two components. At the vertex of the rhombohedra lay nearly regular, strongly interconnected icosahedra. At the center of the rhombohedra is a short chain (Fig. 4). The interatomic bondings are mainly covalent, this conferring the material its electrical and thermo-mechanical properties. The first descriptions assumed the composition of the icosahedra to be B_{12} and the central chain C_3, leading to the B_4C formula. Most recent results [1,7] lead to a more complicated scheme. The icosahedra composition is most often $B_{11}C$, but B_{12} or $B_{10}C_2$ can be found. The central chain is most probably CBC but BBC or BvB (v for vacancy) also exist. This first allows the wide composition range of the boron–carbon phase but since all the configurations have nearly the same ground energy, they may coexist, this leading to an intrinsically disordered solid.

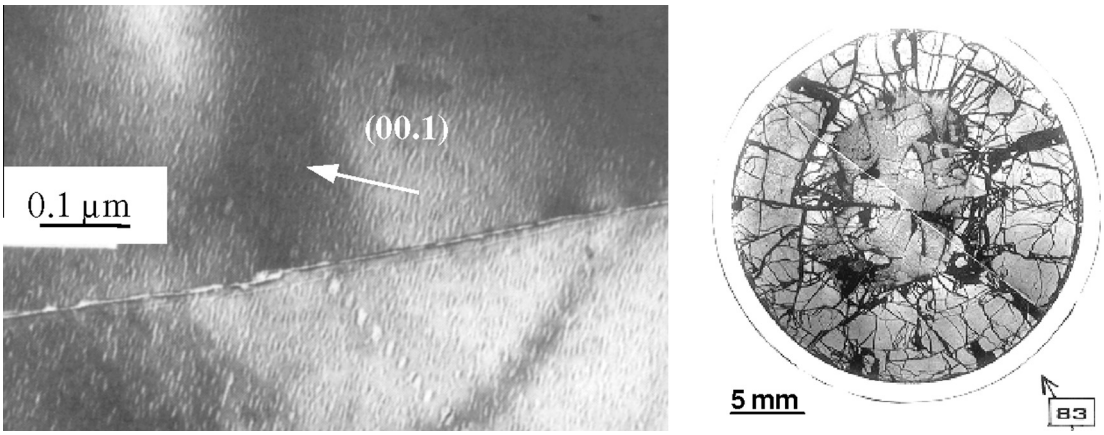

Fig. 3. Boron carbide damage in fast neutron reactor control rods, from [4]. Left: intra- and inter-granular helium accumulation. Right: cracking of absorber pellets in a control rod (French Phenix FBR, boron burnup ~10 at.%).