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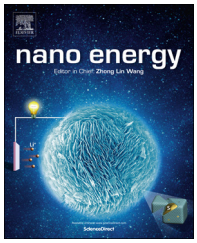

FULL PAPER

Dispersion of carbon nanotubes in aluminum improves radiation resistance

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Abstract

We can mass-produce metal/carbon nanotube (CNT) composites that show improved radiation tolerance. The 0.5 wt% Al+CNT composite showed improved tensile strength without reduction of tensile ductility before radiation, and reduced void/pore generation and radiation embrittlement at high displacements per atom (DPA). Under helium ion irradiation up to 72 DPA, the 1D carbon nanostructures survive, while sp^2 bonded graphene transform to sp^3 tetrahedral amorphous carbon. Self-ion (Al) irradiation converts CNTs to a metastable form of Al_4C_3, but still as slender 1D nanorods with prolific internal interfaces that catalyze recombination of radiation defects, reducing radiation hardening and porosity generation. The 1D fillers may also form percolating paths of "nano-chimneys" that outgas the accumulated helium and other fission gases, and provide an essential solution to the gas accumulation problem.

Nuclear fission and fusion reactors, nuclear waste containment, nuclear batteries and space explorations demand materials with extraordinary thermomechanical properties and radiation resistance. Radiation can induce severe

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damages in materials, including swelling, hardening, creep, embrittlement and irradiation-assisted corrosion [1,2]. The tolerance of radiation damage by structural materials plays a significant role in the safety and economy of nuclear energy [2], as well as the lifetime of nuclear batteries, spaceships and nuclear waste containers, as they are often exposed to long-term radiation [3,4].

Nanostructuring is a key strategy to improve the radiation resistance of materials [5-8]. Carbon nanotubes (CNTs) are well known to be a strong and flexible nanomaterial. If CNTs are uniformly dispersed inside metal as 1D fillers [9-11], its high aspect ratio η (up to 10^8) [12] should create prolific internal interfaces with the metal matrix that may act as venues for the radiation defects to recombine (self-heal). In addition, based on percolation theory and geometrical simulations [13,14], a random 3D network of 1D fillers can form globally percolating transport paths even with diminishing volume fraction $\phi \to 0$, if $\eta \to \infty$. 1D fillers can be efficient for this purpose, considering for example cardiovascular and plant root systems that are 1D transport networks. Helium (alpha particle) accumulation inside materials [15] is a known problem that exacerbates embrittlement and swelling [16]. If the 1D fillers form globally percolating paths of "nano-chimneys" that can outgas the accumulated helium [17] and other fission gases to an external fission-product gettering/trapping system [18], they might provide an essential solution to the problem.

Key questions regarding metal-CNT composite (MCC) in the nuclear environment are:

(1) Does the dispersion of CNTs degrade thermomechanical properties (strength, toughness, thermal conductivity [19], etc.) before irradiation?
(2) Once radiation starts, is radiation embrittlement and swelling reduced (due to self-healing effect of the filler-metal interfaces) in MCC compared to the control metal?
(3) Even if 1D nano-fillers improve (i) and (ii), how stable are these 1D nano-fillers themselves under heavy dose of radiation? Typical radiation exposure to the nuclear fuel cladding material is ~15 DPA (displacements per atom) before they are taken out of the reactor. Core internals in commercial light-water reactors should sustain around 80 DPA after 40 years of plant operations [20], and advanced fast reactors would demand even more.

In this paper we investigate the basic radiation materials science of MCC, in particular Al+CNT composite, using a high-energy ion accelerator to inject He and Al ions which generate atomic displacements in the composite, in lieu of neutrons. We find that in addition to property improvements (i) and (ii), the 1D form factor of nano-fillers does survive up to 72 DPA of He ion irradiation, and also 72 DPA of Al self-ion radiation at room temperature, which is intriguing because every carbon and aluminum atoms are knocked out ~10^2 times, yet the 1D nano-morphologies survive, along with the prolific internal interfaces. The morphological robustness of 1D nano-fillers in non-equilibrium conditions is reminiscent of nanowire growth in chemical vapor deposition that violates equilibrium Wulff construction, and the presence of CNTs in ancient Damascus steel [21] (as the equilibrium phase diagram would indicate that CNTs should be converted to blocky cementite Fe_3C).

We have synthesized Al+CNT composites, as aluminum is cheap and very widely used. Al can be used as the fuel cladding materials in research reactors, as well as containment for nuclear waste, components for robots in radiation environments, etc. It light density may impart significant advantage for space applications. Al has low thermal neutron absorption cross-section of 0.232 barn, above only those of Mg (0.063 barn), Pb (0.171 barn) and Zr (0.184 barn) among structural metals, and high corrosion resistance in water, therefore it is already used widely in low-temperature research reactors [22]. The development of Al+CNT may not only benefit research reactors, but also provide guidance for designing new kinds of cladding materials (e.g., Zr+CNT, Stainless-steel+CNT) that can be used in commercial reactors. Second, Al is used in nuclear battery since it is reflective, and has low production rate of Bremsstrahlung radiation due to low atomic number. Thus it has been recommended for several components in designs of nuclear battery such as shielding, current collector [23] and electrode [24]. Al+CNT will increase the lifetime of nuclear battery because of better radiation resistance. This composite may also alleviate helium accumulation from alpha decay, which is one of the main engineering issues associated with radioisotope thermoelectric generator (RTG) [4].

We have performed accelerator-based ion irradiation tests on Al+CNT (and pure Al control) at room temperature (homologous temperature $T/T_M=0.32$, Al's meting point is $T_M=933.47$ K). At this range, volumetric swelling from void formation becomes prominent when radiation exposure is larger than 10 DPA [2].

Modification of interfaces of 1D nanostructure upon irradiation plays an essential role for MCC properties. Figure 1 provides a schematic illustration of ion beam interaction with CNT. The energies of incoming ions are absorbed and transform CNT structure to rearranged carbon nanostructure, or aluminum carbide nanorods, depending on the ion type and beam energy. The 1D interfaces, if they survive, likely reduce the supersaturation of radiation-generated vacancies, by boosting recombination with self-interstitial atoms (SIA) and interstitial clusters. The light-weight ion irradiation generally generates more "sparse" collision cascades with lower defect density and shorter length compared to heavy ions. Therefore, He ion irradiation causes less Al/C mixing than Al ion irradiation since an interstitial Al atom can quickly find the nearest vacancy of the same chemical species. The CNT undergoes restructuring, making a helical carbon nanostructure, as shown in Figure 1 with a yellow arrow. Irradiation with heavier Al ions, which produce "denser" collision cascades and more Al/C mixing [25], eventually changes the composition of CNT fillers, forming an aluminum carbide phase with 1D nanorod morphology (blue arrow).

For (i), (ii), fabrication of high-quality and low-porosity composite is essential. Achieving uniform CNTs dispersion without inducing degradation to CNTs or Al matrix is the key here. Our specimen preparation consists of three steps (Figure 2A): (step i) declustering of the CNTs on the surface of Al particles, (step ii) encapsulation of the dispersed CNTs and further consolidation into Al particles to form Al-C covalent bonds by spark plasma sintering (SPS), and (step iii) hot extrusion. We used multi-walled carbon nanotubes

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