ABSTRACT

In this work, several scientific problems related to high pressure–high temperature (HP–HT) synthesis of new materials using fullerite as a precursor were studied: first, the mechanism of the transformation of C60 crystal into a nano-clustered graphene phase (NGP) at a pressure of 8 GPa; and second, the effect of disorder introduced into C60 crystals by ball milling prior to HP–HT synthesis on the structure and properties of the NGP. A separate set of experiments was devoted to compression of C60 precursor at unexplored before pressure of 25 GPa and elevated temperatures in search for new type of disordered carbon-based materials.

In the first study, Raman spectroscopy, HRSTEM-EELS, and indentation hardness demonstrate that, under pressure, C60 exhibits a path of transformation from polymerized C60 to NGP. This phase exhibits a short-range order and preferential orientation of nano-clusters of graphene assembled in a highly disordered carbon matrix. In our studies, we observe that the mechanism of C60 transformation into NGP could be understood in terms of nucleation and growth mechanism as opposed to the pseudo martensitic mechanism. Changes in Raman intensity of the Ag(2) C60 mode monitored in polished incompletely transformed carbon particles reveal different steps of transformation. Moreover, the polishing reveals the distribution of shear bands resulting from plastic deformation of the C60 monomer and following the direction of the <110> slip planes in FCC system.

HRSTEM analysis reveals the presence of disorder as an intermediate state between the parent C60 and the nano-graphene units. EELS spectra show that C60 molecules in such state are present as monomers, and the intermediate phase is a sp2–sp3 disordered phase, in which the sp2 fraction is by up to 20% lower than that of graphene nanoclusters. The findings suggest that, after the collapse, the polymer structure breaks down with the formation of a disordered (sp2–sp3) carbon phase containing some fraction of residual C60 molecules. The graphene nanoclusters further nucleate and grow in the intermediate disordered phase. Thus, a nucleation and growth mechanism is proposed for the formation of NGP phase from C60 upon HP-HT action.

For the second problem, highly disordered systems were obtained from ball-milled C60 through HP–HT demonstrating a promising technique to create hard (hardness > 30 GPa) disordered carbons at relatively low pressure (up to 8 GPa).

The nanoarchitecture of NGP and disordered systems was studied using multi-wavelength Raman spectroscopy, HRSTEM, and indentation techniques. The Raman data treatment was carefully studied following the three-stage amorphization trajectory of amorphous carbon. The Raman model consists of G and D bands and data from semi-empirical models that include peak position, FWHM, and intensity ratio. A new approach proposed by the research team includes the presence of carbon pentagons (F band) and carbon heptagons as defects in the graphene clusters and are eventually present in the disordered carbon matrix as well. A peak deconvolution considering the G, D, F and heptagon bands is the model that allows building an empirical correlation between the Raman spectra features and hardness. Using peak deconvolution model based on G, D, F heptagon and sp3 carbon-derived bands allowed us to build an empirical correlation that can be used for a semi-quantitative estimation/prediction of hardness of an arbitrary disordered sp2 carbon-based system based on their spectroscopic (Raman) data.

Finally, experiments on compressed C60 at 25 GPa, previously unexplored pressure, produce superhard 3D-C60 polymers at T below 600 oC temperatures. As the temperature increases, sp3 carbon start dominating the disordered structures. The synthesized materials are semiconductors exhibiting ultra-high hardness that in a particular case exceeds that of single crystalline diamond. UV-Raman spectroscopy reveals a high intensity of T band and a G band position typically observed in tetrahedral amorphous carbon (ta-C)-based thin films. The phase has a residual fraction of sp2 carbons, mainly linear chains and fused aromatic rings.

In summary, the results demonstrate that a whole class of novel materials with outstanding physical properties - superelastic-hard and ultrahard semiconducting carbons can be produced for demanding technological applications at HP-HT by using C60 as a precursor and tuning its microstructure.