11th International Conference on Advanced Materials
Rio de Janeiro Brazil
September 20 - 25
ICAM2009

Influence of experimental conditions on the CNTs nucleation process: multiple nucleation sites on the catalyst particle

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Abstract – The effect of catalytic chemical vapor deposition parameters on the nucleation step of carbon nanostructured materials have been studied. Changes in experimental conditions were able to promote different nucleation mechanisms leading to a multiple nucleation sites around the catalyst particle instead of a typical base- or tip-growth mechanism.

Catalytic chemical vapor deposition (CCVD) process has been used to synthesize carbon nanostructured materials such as nanotubes (CNTs) and nanofibers (CNFs). The role of metal catalyst particles in CCVD syntheses of carbon nanomaterials has been studied and it has been demonstrated that the size of catalyst particles is a critical parameter determining the diameter and other properties of CNTs. However, many important issues are still not clarified such as the effect of the catalyst particles shape among other experimental parameters like carbon precursor concentration on the nucleation process. In this work, catalyst nanoparticles were generated by the deposition of a metal thin film over a silicon substrate followed by annealing to agglomerate the film in separate particles. Carbon nanomaterials were grown in a horizontal tubular quartz furnace at atmospheric pressure and the mechanisms of nanotubes/nanofibers nucleation and growth were analyzed. A new model explaining the nanotube nucleation as a specific instability occurring on the catalyst particle surface supersaturated with carbon has been developed. Besides conventional growth processes, a number of specially designed experiments were carried out to study the effect of various process parameters on the nanotube nucleation and catalyst particle reshaping. The experiments have confirmed the crucial role of microenergetics associated with the process of graphitization during nanotube formation. Experiments realized for supersaturated catalyst particles during different reaction times demonstrated the occurrence of multiple nucleation sites on the catalyst particles. Figure 1(a) shows a scanning electron micrograph for nickel nanoparticles after the exposition to CH_4 (5 pulses of 60 seconds) at 900 ^{o}C. Instead of a normal nanotube nucleation at the particle top, in this case multiple nucleation petals-like sites along the particle circumference can be seen. Tilted SEM image in Fig. 1(b) reveals that carbon segregation occurs at the particle bottom. For longer exposure time (25 pulses of 60 seconds, resulting in a higher carbon concentration), the volume of carbon petals around the particles is bigger (Fig. 1(c)). It was also observed that the number of nucleation sites decreases fast with the particle diameter. The fact that under the present conditions carbon segregation and graphitization do not occur uniformly around the particles indicates the development of some type of surface instability. In these local instabilities, small regions of the supersaturated catalyst particle are involved in multiple isolate nucleation steps and less energy is released compared to a global process involving the entire particle in just one nucleation event. Nevertheless, considerable effect of the local heating due to graphitization must be invoked, as otherwise uniform carbon deposition around the particle should be expected. These experiments have demonstrated that the output of the nucleation process depends on the volume of catalyst particle from which carbon is segregated. These results have shown that in the synthesis of carbon nanostructures using CCVD, parameters like the size of catalyst particles and distribution of carbon inside the particle are of critical importance and have to be considered in the process optimization, along with external parameters as temperature and gas concentration.

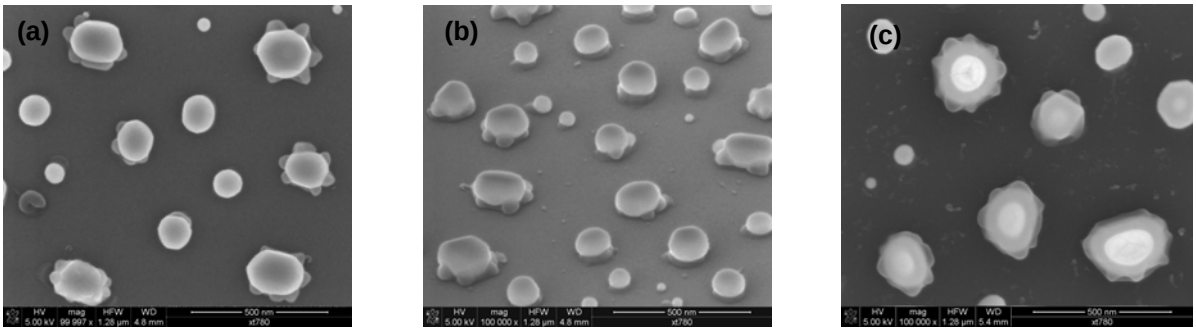

Figure 1: SEM images of multiple nucleation carbon petals-like sites around nickel catalyst particles.