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SYNTHESIS AND MICROSTRUCTURE CHARACTERIZATION OF THE Ni/C_{60} COMPOSITE MATERIALS[1]

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Structural variability of the Ni/C_{60} thin film composites was observed after ion irradiation and/or thermal annealing. Annealing of the irradiated Ni/C_{60}/Ni multilayers led to micrometer-large rod-type particles, annealing of the non-irradiated specimens resulted in truncated rectangular footprints. Micrometer-large spherical or dodecahedral Ni droplets were synthesized by annealing of the non-irradiated Ni+C_{60} mixtures. The structural variation of the Ni/C_{60} systems points out the complex physiochemical processes incited by elevated temperatures. First insight on the microstructural evolution of the Ni/C_{60} composites after ion irradiation and/or thermal annealing is presented in this paper.

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1 Introduction

Since the early nineties, when the method of macroscopic production of C_{60} was established [1], an intensive study of solid C_{60} [2] and related systems [3–5] has been conducted. The scope of the investigation has embraced a variety of fullerene-based composites [6–8] including such 'peculiarities' as polymer/C_{60} mixtures or metal/C_{60} multilayers. It was soon obvious that the C_{60}-based materials exhibit many unusual properties, such as charge transfer between C_{60} and (certain) polymers [9] or strong bonding between C_{60} and (certain) metal surfaces [10], some of which have been already utilized in practical applications [11].

The experimental inspections of the fullerene-related materials have pointed out the strong proclivity of the C_{60} molecules to react with various external reagents and to form complex structures with interesting properties [11]. The fact that the C_{60} molecules were found inbuilt in the structural networks of various multi-elemental complex systems [11–13], gives evidence about the universality of the C_{60} cage, and suggests that new functional materials with C_{60} molecules (as nano-structural building blocks) could be synthesize. This has become a leit-motif of the experimental endeavor of the material scientists in the last decade.

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Ion-irradiation and thermal annealing represent well-established techniques for material processing. Employment of these techniques for the C_{60}-based composites can result in a dramatic alteration of their microstructure, e.g. to fragmentation and transformation of C_{60} to amorphous carbon (a-C). The transformed (a-C based) and original (C_{60} based) systems are structurally different, which may also diversify their basic properties. This aspect is important particularly for the immiscible systems, such as a Ni-carbon allotrope thin film packaging, as it might set in unknown effects during the course of the (thermal) processing [13–15].

This paper reports on the thermal response of the Ni-C_{60} systems (co-mixtures and sandwiches) partly irradiated with energetic ions (to induce disintegration of the C_{60} component) and thermally annealed. The thermal response of the systems was analyzed from the viewpoint of their microstructural alterations.

2 Experimental

The Ni-C_{60} mixtures and sandwiches were prepared by the vapor deposition of Ni and/or C_{60} on the MgO(100) or MgO(111) single crystals. To vaporize the target materials, electron beam bombardment of the 99.9% pure Ni pellets and resistive filament heating of the 99.9% pure C_{60} powder was used. The deposition was performed in the UHV conditions with a typical background pressure $\sim 5 \times 10^{-7}$ Torr.

To prepare Ni/C_{60}/Ni sequential structures with the epitaxially grown buffer Ni and intermediate C_{60} layers (the external Ni layer was polycrystalline), an alternating deposition method with certain deposition kinetics was used, i.e. with deposition rate of both Ni and C_{60} component <5 nm/min, temperature of the substrates 500°C (buffer Ni) or 120°C (C_{60} and external Ni) and thickness of each layer $\sim$300 nm.

The co-mixtures were prepared by the simultaneous evaporation of Ni and C_{60} with the deposition rate (for both Ni and C_{60} components) <5 nm/min. The total thickness of the films was $\sim$300 nm. Temperature of the substrates was kept at 120°C during the co-deposition process.

After deposition, a part of the samples was irradiated by the 7 MeV $^{12}C^{+}$ ions up to a dose $\sim 1 \times 10^{16}$ cm^{-2}. The intensive ion irradiation destroyed $\sim$95% of the C_{60} molecules in the inspected systems and it prompted transformation of the C_{60} fragments towards a-C substance (based on the micro-Raman analysis). Both non-irradiated and irradiated specimens were then subjected to the gradual isochronal annealing (with a typical 100°C / 1hr step) in the Ar + 3%H_2 flow atmosphere up to the temperature 1000°C. The samples were analyzed by scanning electron microscope (SEM) and micro-Raman spectroscopy after each annealing step.

3 Result and discussion

The first results on the structural alteration of the C_{60}/Ni based composites annealed at elevated temperatures can be summarized as follows:

In Fig. 1, the SEM image of the Ni/C_{60}/Ni/MgO(100) sequence annealed up to 1000°C is demonstrated. The high temperature annealing led to the creation of an interesting structural curiosity, i.e. to truncated rectangular 'footprints' (formed across the full thickness of the intermixed multilayer deposit), which are partly self-organized in to the millimeter large circles or tube- like aggregations. The 'footprints' with uniform dimensions of about 5×7 μm^2 are all

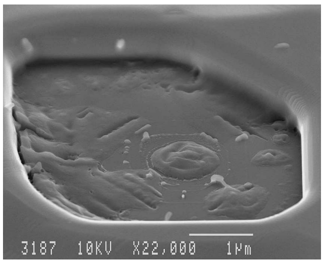

Fig. 1. Truncated rectangular pits.

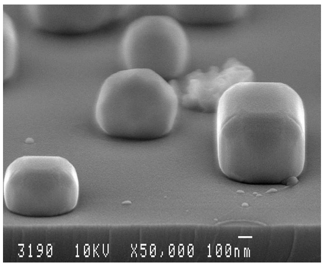

Fig. 2. Rod-type particles.

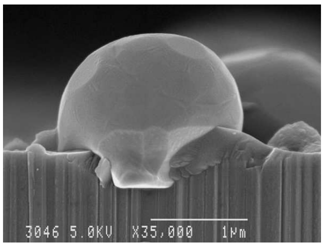

Fig. 3. Ni droplets with a graphitic rind.

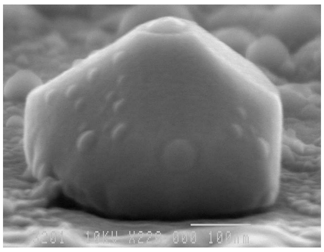

Fig. 4. Ni dodecahedron particles.

oriented according to the crystallographic axes of the MgO(100) substrate. The bottom part of the ’footprints’ has an ornamental structure, which is predominantly made from a-C.

Fig. 2 shows the result of the 1000°C annealing of the irradiated sandwich structure (Ni/a-C/Ni/MgO(100) sequence). It can be claimed, that the evolution of this sample proceeded in a different way. The deposited material re-arranged towards the micrometer-sized rod-type particles, which are slightly anchored in the substrate. The particles are well separated and also oriented according to the crystallographic axes of the MgO(100) substrate. The particles have a dominant Ni core, which is covered by a thin graphitic layer.

Fig. 3 represents the result of thermal annealing of the non-irradiated mixture Ni+C$_{60}$ deposited on MgO(100). After multi-step thermal processing up to 1000°C, massive spherical faceted droplets with the Ni core and graphitic rind were formed. The droplets with a diameter up to 2 μm are deeply (up to $\sim$400 nm) anchored into the substrate and are surrounded by the MgO crystallites.

The annealing of the non-irradiated mixture deposited on MgO(111) led to the creation of the dodecahedron particles with the sub-micrometer scale (see Fig. 4). The dodecahedrons were grown on an expense of the Ni-(a-C) substance which similarly, as in the previous case (see Fig. 3), forms the environment around the particles. The dodecahedrons have a massive hexagonal base, which tapers in the upper part into the pyramidal shape. On the surface of the particles small ‘navels’ are also seen. They protrude in the spots, which correspond to the directions of the main crystallographic axes.

The mechanism of the structural artefacts’ formation (introduced above) is not clear. However, as discussed in [14], both components C$_{60}$ and Ni are immiscible partners that tend to separate if they are mixed together. During thermal annealing the stressed structure can relax via complex mechanism triggering (i) out-diffusion of the C_{60} molecules, (ii) fragmentation of their cages, (iii) rearrangement of fragments to amorphous carbon (a-C), (iv) Ni and carbon nanostructure phase formation, (v) separation, (vi) self-organization, etc. The whole process also depends on the substrate that can work (in case of monocrystal) as a template where Ni (but also C_{60}) can nucleate and accommodate the texturing (e.g., cube-on-cube texturing in case of MgO(100)). In such a way, the rod-type and dodecahedron Ni particles or Ni droplets with a graphitic covering can be synthesised. In case of truncated rectangular pits, their creation might originate in localities where a-C clusters are formed. The a-C clusters segregate and coalesce, so the walls of the pits become Ni-rich, which may result in the accommodation of their orientation according to the crystallographic axis of the substrate.

4 Conclusion

In conclusion, it was observed that thermal processing has a profound effect on the structural evolution of both multilayer and co-mixture Ni-C_{60} systems (whether irradiated or non-irradiated). The transformation of C_{60} to a-C (by ion irradiation) results in a diversification of the structural evolution during thermal annealing. The token of the multi-structural features gives evidence of the complex interplay between transitional metals, fullerenes and amorphous carbon performed on the flat surfaces of the ionic crystals.

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