

The growth of a polycrystalline graphene from a liquid phase.

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ABSTRACT

The preparation of polycrystalline graphene from the liquid phase has been discussed. This method will be used for technology fabrication of functional nanocomposite materials to be applied as reversible hydrogen storage. The novelty of the presented paper is the mechanism of graphene growth from the liquid phase on the Cu-Ni alloy and the type of atmosphere, which was used in the graphene fabrication - acetylene, ethylene, hydrogen. Stages of nucleation and polycrystalline growth of graphene were identified. The proposed mechanism of the studied phenomena and processes were discussed. The effects of cleaning-zone were observed and confirmed. Furthermore the paper presents the results of a single- and multi-layered graphene growth phase. It is assumed as a the final result the optimalization of the industrial-scale production of low-cost polycrystalline nanocomposite based on graphene will be done, considering already mentioned applications.

Keywords: graphene growth, polycrystalline graphene, liquid phase

1 INTRODUCTION

It is expected composite materials based on graphene will become more and more popular and commonly used. The main reasons of such trend could be their good strength and physico-chemical properties. Moreover, nowadays graphene can be synthesized via several well-known methods [1-10].

Methods of graphene synthesis could be classified according to the employed techniques, which were already reported in the literature, namely published and granted patents. Based on this analysis (Fig. 1) it is quite evident that substantial patenting activity is directed towards the development of CVD and exfoliation techniques.

This paper refers to the original method, which is based on graphene synthesis from the liquid phase [11]. This method will be used for fabrication of functional nanocomposite materials to be applied as reversible hydrogen storage. Developed new nanomaterials could be potentially used as parts of technological installations for heat and thermo-chemical treatment where hydrogen is a process medium or is used in high pressure gas quenching

(HPGQ) systems [12, 13]. Moreover, it is expected such materials, when reaching the critical threshold of 6.5% wt. hydrogen absorption on an industrial scale, will be used for the storage of hydrogen in the vehicle of the future [14].

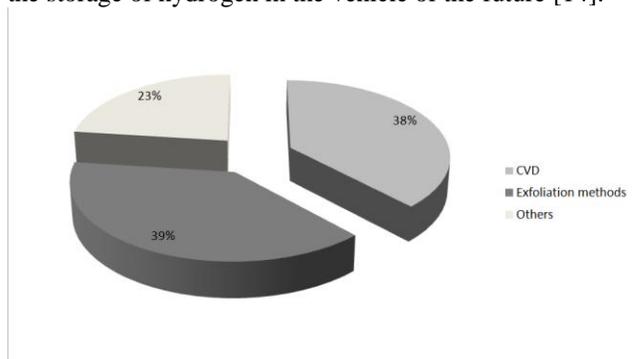


Figure 1. Segmentation of graphene synthesis methods. [Center for Knowledge Management of Nanoscience & Technology - CKMNT]

2 INVESTIGATION

Copper-nickel alloy was used as a substrate for the production of graphene (Fig. 2). Nucleation and growth steps took place in the liquid phase. The mixture of acetylene, ethylene, and hydrogen in the ratio of 2:2:1 was used as a carburizing medium in the temperature range of 1250 ÷ 1200 ° C (2282 ÷ 2192oF) [15]. SEM images shown below were taken at stages of nucleation and growth. Different cooling rates after carbon saturation were applied, namely in the range from a few to fractions of a degree per minute.



Figure 2. The substrate chemical composition: Cu – 72%, Ni – 28%. EDS spectrum.

Depending on the process parameters nucleation and growth stages of a single multi-layer polycrystalline graphene sheets were observed (Fig. 3).

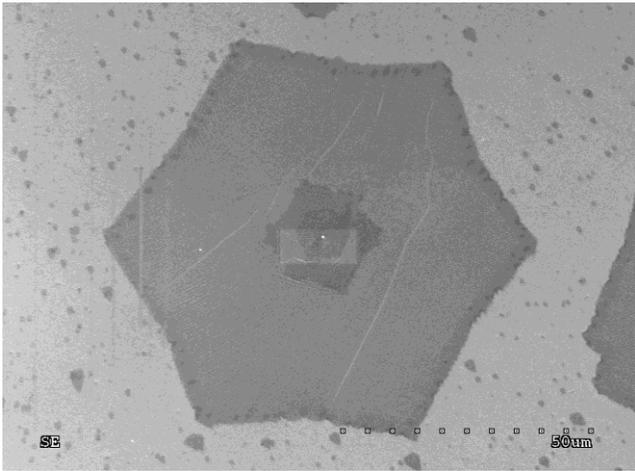


Figure 3. The nucleation and growth of a polycrystalline multilayer graphene. SEM image.

Additionally, growth of polycrystalline graphene monolayer was also observed (Fig. 4). It can be assumed the formed grain boundaries could be classified as a small angle type.

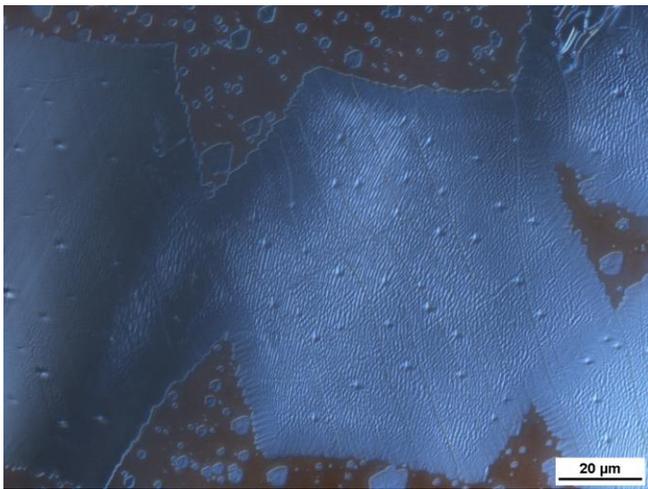


Figure 4. The polycrystalline graphene - Nomarski interference contrast image.

Depending on the cooling conditions and other process parameters, it was possible to obtain different particle size (Fig. 5, 6). The content of those particles also varied.

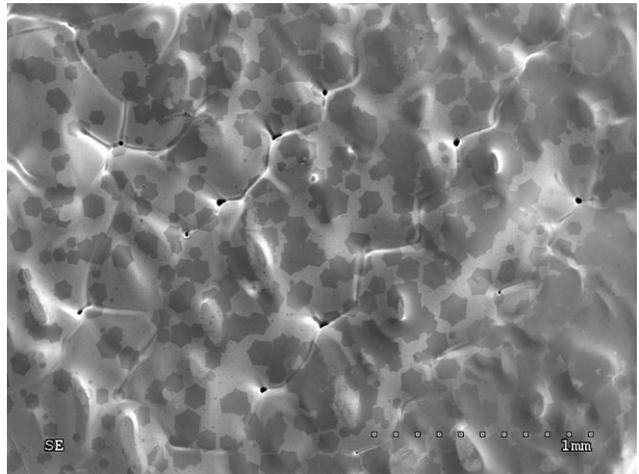


Figure 5. The polycrystalline graphene. SEM image.

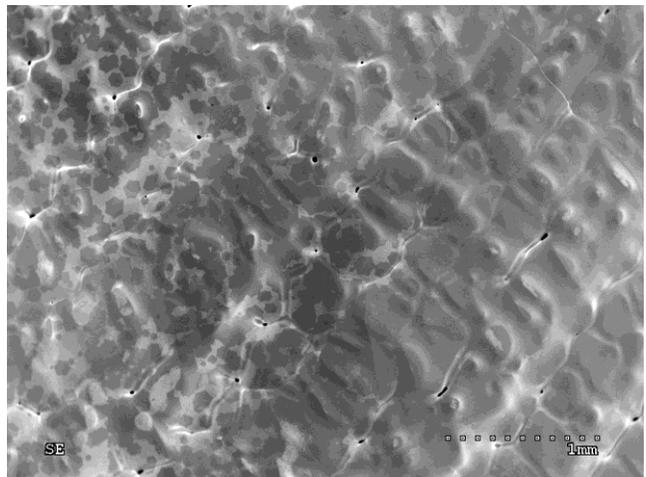


Figure 6. The polycrystalline graphene. SEM image.

Simply by changing the process conditions it was possible to select the optimum process parameters. As a result continuous uniform coatings of polycrystalline graphene with determined and adjusted number of layers could be obtained (Fig. 7).

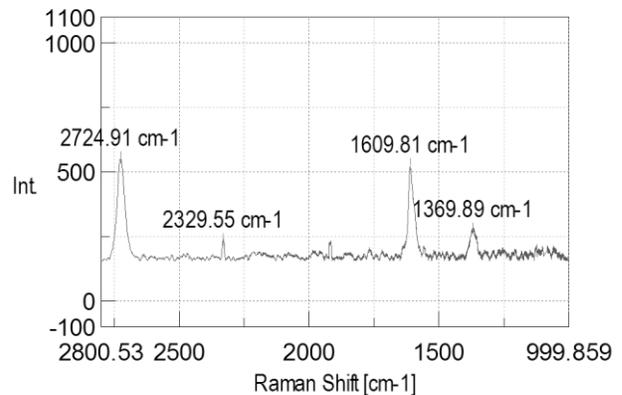


Figure 7. Raman spectra.

Synthesized graphene was examined by Raman spectroscopy. Raman spectra were recorded in the range of

1000 – 3000 cm^{-1} using visible – 2.33 eV (532 nm) excitation of Ar^+ laser. The scattered light was dispersed by JASCO NRS 5100 spectrometer working on backscattering mode. The laser beam was focused on 30 μm in diameter spots. Spectral resolution of measurements was 1 cm^{-1} . The Raman spectra confirmed the presence of graphene. Three prominent peaks were observed, namely the peak around 1350 cm^{-1} called D band, the G band $\sim 1582 \text{ cm}^{-1}$, and the G' band $\sim 2700 \text{ cm}^{-1}$. The peak around 2330 cm^{-1} was also detected but that comes from Raman mode of N_2 gas present in the air surrounding the sample[16].

In the case of processes, which were done in the liquid as well as in the solid state, zone-cleaning effect was detected (Fig. 8). Traces of impurities were pushed by the crystallization front toward the border regime. Eventually, the incorporation of impurities occurred only in the solid phase.

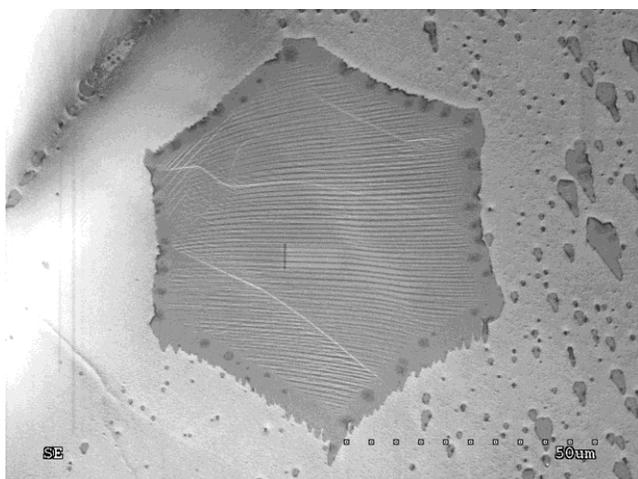


Figure 8. The zone-cleaning effect. SEM image.

3 SUMMARY

The obtained results confirmed the reported method of graphene manufacture from the liquid phase could be successfully used. The intermediate structures could be also synthesized. Due to that it was possible to study the mechanisms of graphene nucleation and growth. Moreover this technique allowed to produce large graphene panels, so they will provide a base for the production of nanocomposites targeting hydrogen storage applications.

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