SYNTHESIS OF CARBON NANOFIBERS BY ETHYLENE PYROLYSIS OVER Mg_2Ni

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Introduction

For the synthesis of carbon nanofibers (CNF) and nanotubes (CNT) in the processes of caatlytic decomposition of hydrocarbons nickel catalysts are widely used [1]. As the diameter of such carbon tubular products essentially depends on the size of catalytic particles [2,3], to synthesize CNF and CNT of less thickness the presence of nickel catalyst in the form of nanosized metal particles is required in the reaction zone, and the particles being not subjected to agglomeration and sintering. To reach this goal the catalytic process could be performed in such a way when metal nickel particles to form immediately in the reaction zone, as it was done in the work of CNF synthesis by decomposition of hydrocarbon gases over intermetallic compounds of La and Ni [4]. Here the initial intermetallide served as a procatalyst for nucleation and growth of CNF.

In the present work the CNF synthesis is performed by ethylene pyrolysis in the presence of intermetallide Mg_2Ni. The work is aimed at finding correlation between process parameters (etmperature, gas phase contents) varied in a wide range and the contents of carbonaceous products.

The obtained carbon nanofibers were used for the synthesis of composite materials MgH_2–CNF, whose hydrogen storage characteristics were thoroughly studied.

Experimental

The pyrolysis of ethylene was carried out in a horisontal gas flow reactor at 0.1 MPa in the presence of fixed bed powdered (average particle sizes 1–10 mkm) intermetallide Mg_2Ni lying as a thin stratum having the thickness of 0.3 mm and the mass of 0.1 g in all experiments. The gaseous mixtures $C_2H_4/H_2/Ar$ were feeded at various ratios. The feed rate of ethylene was constant in all experiments – 40 cm^3/min, as well as the total flow rate of the gas mixture – 140 cm^3/min. The gas phase contents was varied by changing the flow rate of H_2 and Ar within the range of 0–100 cm^3/min. The detailed description of the experiment is provided elsewhere [3]. The duration of the process was 1 h in all experiments. The only soot formed during 1 h on the surfece of powdered intermetallide was taken into account while determing the mass of carbon products of the pyrolysis.

The products of the pyrolysis were studied by means of transmission electron microscopy, X-ray diffraction and chemical analyses.

Results and discussion

According to the chemical analysis data the hydrogen content in the synthesis products is less then 0.5 mass. %, while Mg : Ni ratio being close to the initial contents of the intermetallide. X-ray diffraction analysis of the synthesis products evidence the presence of metallic nickel particles (d = 2.04, 1.76 Å), graphitized structures (d = 3.39 Å) (fig. 1). This means that during the pyrolysis of ethylene the initial intermetallide decomposes to form nickel particles. On the laters the process of nucleation and growth of soot carbonaceous products proceeds.

A noticable soot formation was at temperatures as low as 400°C. The maximal yield of the soot was at 500°C. With further increasing the pyrolysis temperature the soot mass decreases due to coking of the work surface of catalytic particles. Dilution of the feeded gases with hydrogen causes the increasing in the soot mass (Tabl. 1). Hydrogen seems to interact with coke precursors C_xH_y (x = 1, 2; y = 1, 2, 3), adsorebd on the surface of nickel particles to move them back to the gas phase thus decreasing the amount of amorphous carbon and increasing that of structured carbon fibers. It is clear that further increase of the hydrogen content leads to decrease of the total yield of the soot. The gas mixture contents of $C_2H_4 : H_2 : Ar = 1 : 1.25 : 1.25$ was determined to be the optimal one for the total yield of the soot.

Tabl. 1. Mass of the formed soot (g/g Mg_2Ni) at various temperatures of C_2H_4 pyrolysis (feed rate 40 *cm3/min*) and Ar : H_2 ratios.

Gas flow rate, cm^3/min		Temperature, °C			
Ar	**H_2**	**500**	**600**	**700**	
100	**0**	0.44	0.15	0.20	Mass, g
75	**25**	6.52	6.55	1.04	
50	**50**	13.44	6.80	0.81	
25	**75**	11.60	9.67	0.94	
0	**100**	11.68	12.27	1.91	

The transmission electron microscopy of the pyrolysis products shows the presence of carbon fibers having the outer diameter of 20–200 nm, and some of them, the thinest, having hollow channel inside. The most of fibers are a kind of tightly curled helices or "plumed clouds".

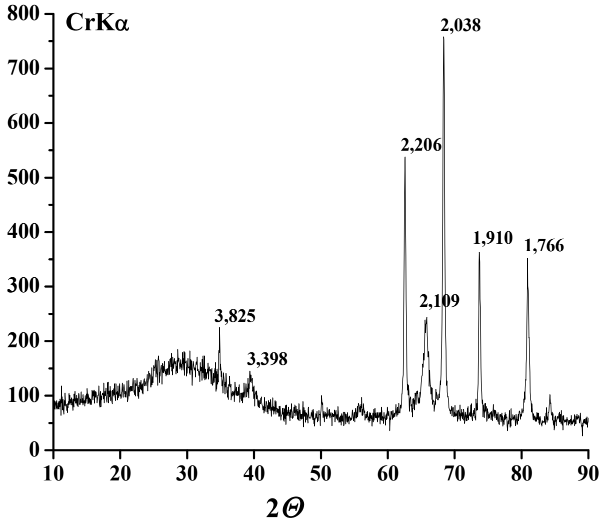

Fig. 1. X-ray diffractogram of the pyrolysis products synthesized at 700°C.

The study of hydrogen sorption properties of the MgH_2-CNF composites, obtained by mechanochemical treatment of mixtures of the components evidences that carbon nanofibers are perspective for preparation of hydrogen storage composite materials.

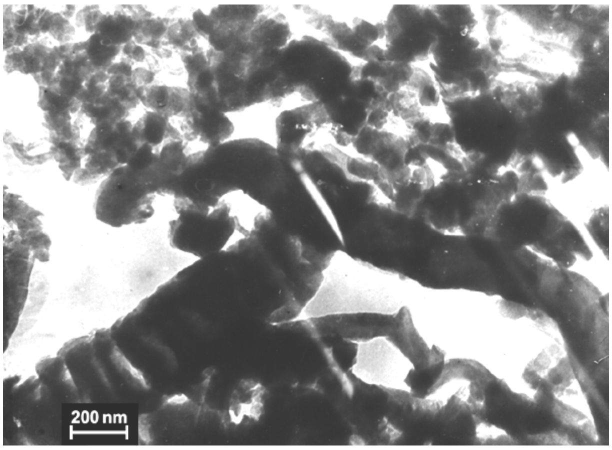

Fig. 2. TEM image of the sample obtained at 600°C.

Conclusions

Powdered intermetallide Mg_2Ni is an effective procatalyst for synthesis of CNF.

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