Development of Porous Graphitic Carbon Materials by Spark Plasma Sintering and Selective Dissolution Using Fe-Subgroup Metals as Graphitization Catalysts and Space Holders

In this work, carbon-based materials were obtained by graphitization-accompanied sintering of mixtures containing non-graphitic forms of carbon (nanodiamonds or amorphous carbon) and nickel, iron or cobalt as graphitization catalysts. The influence of the nature of the metal catalyst and the initial carbon source and the conditions of Spark Plasma Sintering and post-dissolution high-temperature annealing on the phase composition, structure, and properties of the porous carbon materials was investigated.

Porous graphitic materials with high graphitization degrees, high specific surface area, stable pore structure and mechanical robustness are attractive from the practical point of view as electrode materials for electrochemical devices. The purpose of this research was to evaluate the possibilities of producing porous graphitic carbon, including self-standing 3D objects, by conducting graphitization in the bulk state during Spark Plasma Sintering in the presence of Fe-subgroup metal catalysts, also playing a role of space holders, followed by selective dissolution of the metal, and gain an understanding of the influence of the processing variables (nature of the metal catalysts selected from Fe-subgroup metals and initial carbon source, Spark Plasma Sintering conditions, post-dissolution high-temperature annealing) on the phase composition, structure and properties of the porous carbon materials.

The graphitization degree of the amorphous carbon or nanodiamonds in the presence of nickel or cobalt increased with increasing SPS temperature. The iron-containing mixtures showed the formation of the iron carbide Fe_3C phase after the SPS. The degree of graphitization of porous materials obtained from the iron-containing compacts did not depend on the sintering temperature.

It was found that SPS of nanodiamonds in the presence of nickel leads to a dramatic decrease in the SSA of the carbon-based material. The presence of nickel enhanced the graphitization process and accelerated growth of the graphite crystallites. At the same time, it was not possible to detect any trend in the changes of the SSA of the carbon-based materials obtained after nickel has been dissolved from the Ni-C_{am} compacts. The SSA of the porous materials obtained from the Fe-C_{am} compacts remained practically unchanged in the compacts sintered at different temperatures. In the case of system Co-C_{am}, the SSA increases with increasing sintering temperature.

According to the Raman spectra and I_D/I_G of the samples, in which Ni and Co were used as graphitization catalysts, the graphitization degree increases with increasing sintering temperature. Increasing holding time did not enhance graphitization. The shape of the Raman spectra of the samples obtained from the Fe-C_{am} compacts shows little variation with the sintering temperature. From the presence of pronounced D-bands in the spectra, it can be concluded that the product of partial dissolution of iron from the compacts contained carbon that was poorly graphitized.

This work has shown that sintering of amorphous carbon and nanodiamonds in the presence of nickel or cobalt induces both graphitization and growth of graphite crystallites. Sintering of non-graphitic carbon in contact with iron presents a more complicated situation, in which it is not possible to transform carbon introduced into the initial mixture quantitatively into graphite due to the formation of the Fe_3C phase.

The formation of carbon nanotubes on the surface of diamond crystals catalyzed by nickel was investigated.

The results of the project have been presented in the following publications:

1. Multiwalled carbon nanotube forests grown on the surface of synthetic diamond crystals/ B.B. Bokhonov, A.V. Ukhina, D.V. Dudina, H. Katsui, T. Goto, H. Kato // Ceramics International 43 (2017) 10606–10609.

2. Structural characterization of carbon-based materials obtained by Spark Plasma Sintering of non-graphitic carbon with nickel and iron as catalysts and space holders/ A. V. Ukhina, B. B. Bokhonov, D. V. Dudina, K. Yubuta, H. Kato // Ceramic Transactions, 2017, accepted.

3. Morphological features of W- and Ni-containing coatings on diamond crystals and properties of diamond-copper composites obtained by Spark Plasma Sintering/ A. Ukhina,

B. Bokhonov, D. Samoshkin, S. Stankus, D. Dudina, E. Galashov, H. Katsui, T. Goto, H. Kato// Materials Today: Proceedings, 2017, accepted.
4. The influence of the formation of Fe_3C on graphitization in a carbon-rich iron-amorphous carbon mixture processed by Spark Plasma Sintering and annealing/ Dina V. Dudina, Arina V. Ukhina, Boris B. Bokhonov, Michail A. Korchagin, Natalia V. Bulina, Hidemi Kato// Ceramics International, 2017, accepted

Table 1. The fabrication conditions and characteristics of the carbon-based materials obtained by SPS of metal-carbon mixtures followed by selective dissolution of the metal: composition of the initial metal-carbon mixtures, sintering temperature and holding time, apparent density of the sintered metal-carbon compacts, specific surface area of the carbon based materials and I_D/I_G ratio of the corresponding Raman spectra of the carbon-based materials.

Metal-carbon powder mixture	**SPS temperature, °C**	**Holding time, min**	**Apparent density, g·cm^{-3}**	**I_D/I_G**	**SSA, m^2/g**
Ni-C_{nd}	800	3	4.94	0.86	240
Ni-C_{nd}	800	10	4.98	0.95	180
Ni-C_{nd}	1000	3	5.94	0.21	20
Ni-C_{am}	500	10	3.63	0.78	42
Ni-C_{am}	600	10	4.07	0.68	28
Ni-C_{am}	700	10	4.29	0.64	57
Ni-C_{am}	800	10	5.11	0.55	44
Ni-C_{am}	1000	10	5.22	0.31	16
Fe-C_{am}	600	5	3.28	0.85	51
Fe-C_{am}	800	5	3.33	0.84	57
Fe-C_{am}	900	5	3.77	0.90	55
Co-C_{am}	800	3	4,5	0.87	80
Co-C_{am}	1000	3	5,11	0.80	62

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