Short communication

Structural and morphological transformations in cobalt-carbon mixtures during ball milling, annealing and Spark Plasma Sintering

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ABSTRACT

In this work, powder mixtures of cobalt and amorphous carbon of the Co-17 wt%C composition were processed by high-energy ball milling and annealing/Spark Plasma Sintering in vacuum to study the morphological transformations associated with graphitization of carbon in the powder and consolidated states of the material. High-energy ball milling led to the hcp-fcc transition in cobalt. During annealing of the milled powder, cobalt nanoparticles were encapsulated in graphitic shells. In the consolidated state, graphitization of carbon resulted in the formation of a 3D graphitized structure. Cobalt remained as the fcc phase in the annealed powders and sintered compacts due to the stabilizing action of graphitic shells and graphitic 3D walls, respectively. Selective dissolution of cobalt allowed obtaining porous graphitic materials composed of platelet-shape crystallites 20 nm thick. The specific surface area of the porous graphitized materials obtained from the compacts sintered at 800–1000 °C was of the order of $100\,\mathrm{m}^2\,\mathrm{g}^{-1}$.

In recent years, extensive research has been devoted to the processes of graphitization and fabrication of carbon structures of different morphologies in the presence of Fe-subgroup metals [1–7]. The formation conditions of metastable phases and their role in the overall graphitization process in carbon-Fe-subgroup metal systems have been addressed in a number of studies [3,4,7,8]. Despite success in gaining control over the morphological characteristics of the synthesized structures, many questions related to the fundamental aspects of the interaction between carbon and Fe-subgroup metals are still unanswered. From the practical standpoint, sintering/consolidation of carbon-rich metal-carbon mixtures is of great interest, as it allows obtaining bulk metal-carbon materials. In the consolidated state, metal-carbon materials and carbon materials derived from them possess several advantages, which include easier handling and higher durability in comparison with powders. In porous carbon materials, functional properties can be achieved along with a desired level of mechanical strength [9]. In consolidated graphitized nanodiamond compacts, an order of magnitude increase in electrical conductivity was achieved relative to the powder state (non-sintered graphitized nanodiamonds) [10].

Porous carbon materials can be derived from metal-carbon alloys or composites by the dealloying [11] or selective dissolution [6]

techniques. The porous structure of carbon formed with the help of space holders will depend on the size, morphology and chemical nature of the space holder. In our recent studies, we have evaluated nickel and iron as graphitization catalysts and space holders to produce porous graphitic materials by selective dissolution of the metals from the Spark Plasma Sintered compacts [6,7]. Cobalt-carbon is another system, which draws significant attention in the area of development of functional carbon materials [12–19]. Yang et al. [13] report the fabrication of nanocomposites with high electrochemical hydrogen storage ability by ball milling of cobalt-graphene mixtures. In a study by Tynan et al. [19], 3D graphene foams were formed from methane in a chemical vapor deposition process, in which a porous cobalt oxide structure (formed from a dextran-cobalt gel) served a substrate and supplied a catalytically active element for the synthesis of graphene.

To our best knowledge, the sintering behavior of ball-milled cobalt-amorphous carbon mixtures has not been previously reported. During heat treatment of amorphous carbon in the presence of cobalt, graphitization should be expected, the morphology of graphitic structures depending on the mutual arrangement and size of the metal and carbon particles. The aim of the present work was to study the structural changes occurring in both carbon and metal phases in powder mixtures subjected to ball milling, annealing and consolidation by Spark Plasma

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Sintering (SPS). This consolidation method was chosen for its capability to achieve densification under conditions of limited grain growth [20]. The morphological features and specific surface area of graphitized porous materials obtained by selective dissolution of cobalt from the sintered compacts are reported. For the first time, cobalt is evaluated as a catalyst acting also as a space holder for the synthesis of porous graphitic materials.

Powders of cobalt (electrolytic, PK-1u, 99.35% purity, particle size < 71 μm) and amorphous carbon (carbon black PM-15, 95% purity, particle size 100–200 nm [4]) were used as the starting materials. A Co-17 wt%C mixture was ball-milled in a high-energy planetary ball mill AGO-2 under an argon atmosphere for 1–10 min. AGO mills (abbreviation from the Russian "activator water-cooled") were developed at the Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, Russia. The ball to powder weight ratio was 20:1. The centrifugal acceleration of the milling balls was $600\,m\,s^{-2}$. Two stainless steel vials with a volume of $135\,cm^3$ each were used. Stainless steel balls 8 mm in diameter were used as the milling media.

Annealing of the ball-milled mixtures was conducted in vacuum at 320 °C, 520 °C and 720 °C for 1 h. Consolidation of the mixtures was carried out using a SPS Labox 1575 apparatus (SINTER LAND Inc., Japan). A graphite die with an inner diameter of 10 mm and tungsten punches were used. Graphite foil was used to prevent sticking of the samples to the die and punches. The temperature was controlled by a pyrometer focused on a hole in the die wall at its mid-plane. The heating rate was $50\,°C\,min^{-1}$. The powders were sintered at 800 and 1000 °C. The samples were held at the maximum temperature for 3 min. A uniaxial pressure of 40 MPa was applied. Consolidation was conducted in dynamic vacuum at a residual pressure of 10 Pa. Disk-shaped pellets with a thickness of 3 mm were produced.

The apparent density of the sintered compacts was determined by measuring the weight of samples and their dimensions. For conducting structural studies of the graphitization products, the sintered samples were placed in 10% HCl solution for 48 h to dissolve metallic cobalt.

The phase composition of the samples was investigated by X-ray diffraction (XRD) using a D8 ADVANCE diffractometer (Bruker AXS, Germany) with CuKα radiation. The structure of the annealed powders was observed by Transmission Electron Microscopy using a JEOL JEM 2000 FX II microscope working at an accelerating voltage of 200 kV. The microstructure of the sintered Co−C compacts and porous graphitized samples was studied by Scanning Electron Microscopy using a ULTRA 55 microscope (Carl Zeiss, Germany). The structure of the porous graphitized materials was also studied by Raman spectroscopy using an inVia confocal Raman microscope (Renishaw, New Mills, UK) with an excitation wavelength of 532 nm. The specific surface area of the porous graphitized materials obtained after cobalt had been dissolved was determined from nitrogen adsorption-desorption isotherms at 77 K by the Brunauer–Emmett–Teller method.

The stable phase of cobalt at room temperature is hexagonal close-packed (hcp) [21]. According to the Co−C phase diagram, the equilibrium phases for the Co-17 wt%C composition are hcp-Co and graphite [22]. The transition from the hcp to face-centered cubic (fcc) phase occurs at 422 °C (eutectoid temperature); the estimated equilibrium solubility of carbon in cobalt at this temperature is $8.74 \cdot 10^{-4}$ at.%. Upon ball milling, transformations between the hcp and fcc phases of cobalt are possible and depend on the milling intensity [23]. In the present study, co-milling of cobalt and amorphous carbon led to the formation of the fcc phase. Fig. 1 demonstrates XRD patterns of the initial Co-17 wt%C mixture and those of the mixtures milled for 1, 3 and 10 min. The initial cobalt powder contains both hcp and fcc phases. During ball milling, hcp-Co gradually transforms into the metastable nanocrystalline fcc-Co phase, as can be concluded from the increasing peak intensities of this phase with the milling time. One of the possible reasons for the formation of the fcc phase during milling is a temperature rise in the milling vials under high-energy treatment conditions. Another possibility is the forced introduction of carbon into the

hcp-Co lattice during high-energy ball milling and the formation of unstable phases, which, upon partial relaxation, transform into the fcc carbon-containing structure, as carbon has a much higher solubility in fcc-Co than in hcp-Co. Previous studies have suggested that a small grain size may be responsible for the stabilization of the metastable fcc-Co at room temperature (see Ref. [23] and references therein).

Annealing of the ball-milled mixtures led to graphitization of carbon, the graphitization degree increasing with the annealing temperature (Fig. 2). The (002) reflection of graphite is not yet detectable on the XRD pattern of the mixture annealed at 320 °C, but clearly appears on the pattern of the powder annealed at 520 °C. The TEM analysis shows that during annealing of the ball-milled mixture at 720 °C, graphitic shells form on the surface of cobalt nanoparticles (Fig. 3). It can, therefore, be concluded that graphitization of carbon on the surface of cobalt resulted in the formation of graphite-encapsulated metal nanoparticles.

In Ref. [24], a stabilizing effect of graphite shells on the metastable phases contained in the cores of core-shell structures was addressed: metastable fcc-Co and tetragonal ZrO_2 were preserved at room temperature in the form of nanoparticles surrounded by graphitic shells. Using ZrO_2 as an example, Pol et al. synthesized a product consisting of separate particles of carbon and ZrO_2 and found that the latter was mostly monoclinic (stable phase) [24]. Consequently, encapsulation played a critical role in the preservation of the metastable phase in the particles. In the present work, the fcc phase was retained after annealing of the ball-milled powder mixtures. The influence of graphitic shells on the crystalline structure of encapsulated cobalt can be rationalized by considering graphite as a diffusion barrier for the metal. Covered with several layers of graphite, particles of cobalt are not prone to coalescence or growth. Therefore, even in the annealed state, cobalt remains in the form of nanoparticles while the metastable fcc phase is preserved owing to the size effect noted above.

In carbon-Fe-subgroup systems, the formation of graphitic carbon is mediated by the metal. Indeed, in our earlier work [4], we suggested that dissolution of carbon in the metallic catalyst (in the Ni-amorphous carbon system) or the formation of a metastable carbide (in the Fe-amorphous carbon system) are the processes enabling the transformation of amorphous carbon into graphite. According to Marshall & Wilson [12], in ball-milled mixtures of cobalt and graphite, cobalt acted to form an unstable phase, which decomposed during annealing. While studying the crystallization behavior of amorphous films produced by co-sputtering of cobalt and carbon, Konno & Sinclair [2] found that, during heating of the films up to 500 °C, graphite cannot form directly from the amorphous state. The precipitation of graphite was preceded by the formation of a cobalt carbide phase. In C-rich films containing more than 40 at.% of carbon, crystallization resulted in the formation of hcp-Co and amorphous carbon, which was attributed to the inability of the system to form a carbide phase at these concentrations of carbon.

Spark Plasma Sintering of the ball-milled Co-17 wt%C powder led to graphitization of carbon and densification of the material. Fig. 4 (a) shows XRD patterns of the compacts obtained by SPS of the ball-milled mixture at 800 and 1000 °C. The size of cobalt crystallites in the sintered compacts determined by the Scherrer equation is 40 nm. Similar to the annealed samples, the fcc phase of cobalt was preserved after SPS, the network of (partially graphitized) carbon playing the stabilizing role by slowing down the growth of the metal crystallites. Both XRD patterns (Fig. 4 (b)) and Raman spectra (Fig. 4 (c)) of the porous graphitized materials obtained by selective dissolution of cobalt from the sintered compacts show that graphitization of carbon occurred during sintering, its degree increasing with the sintering temperature. The I_D/I_G intensity ratio of the Raman spectra is 0.87 and 0.81 for the porous carbon obtained by selective dissolution of cobalt from samples sintered at 800 and 1000 °C, respectively. This indicates enhanced graphitization at a higher temperature. The XRD pattern of the initial amorphous carbon powder is provided (Fig. 4 (b)) to allow comparison to be made with the graphitized samples.