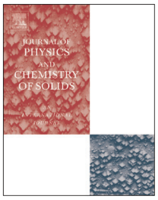
Journal of Physics and Chemistry of Solids 76 (2015) 192–202

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



Formation of self-supporting porous graphite structures by Spark Plasma Sintering of nickel–amorphous carbon mixtures

Boris B. Bokhonov [a], Dina V. Dudina [a,*], Arina V. Ukhina [a], Michail A. Korchagin [a], Natalia V. Bulina [a], Vyacheslav I. Mali [b], Alexander G. Anisimov [b]

[a] *Institute of Solid State Chemistry and Mechanochemistry SB RAS, Kutateladze Street, 18, Novosibirsk 630128, Russian Federation*
[b] *Lavrentiev Institute of Hydrodynamics SB RAS, Lavrentiev Avenue, 15, Novosibirsk 630090, Russian Federation*

ARTICLE INFO

Article history:
Received 23 April 2014
Received in revised form
22 July 2014
Accepted 16 September 2014
Available online 19 September 2014

Keywords:
A. Metals
C. Electron microscopy
C. X-ray diffraction
D. Microstructure

ABSTRACT

Graphitization of amorphous carbon in the presence of nickel has been reported for various configurations of the metal–carbon interface; however, no study has been performed to evaluate a possibility of forming self-supporting networks by sintering of the *in situ* formed graphite. In this work, we have shown that Spark Plasma Sintering (SPS) of nickel–amorphous carbon mixtures containing 50 vol% of Ni at 1000 °C results in the formation of networks formed by sintered graphite platelets 50–200 nm thick and 0.3–2 μm in diameter. Upon selective dissolution of nickel, a self-supporting porous 3D skeleton was revealed in 20 mm-diameter compacts. Starting from the mechanically milled Ni–C mixture, porous graphite of uniform microstructure and containing submicron pores was obtained. A model study has been performed, in which a thin amorphous carbon film graphitized during annealing and formed a continuous graphite film with micron-sized grains covering an area of 2 cm × 2 cm of the surface of a Ni foil. We discuss the role of the *in situ* formation of graphite by nickel-assisted graphitization in the formation of networks consisting of well sintered platelets during the SPS and the design possibilities of porous carbon materials produced by phase separation in nickel–graphite composites.

1. Introduction

Low-temperature graphitization of amorphous carbon in the presence of nickel has been known and utilized for several decades [1–5]. It is generally accepted that nickel acts as a graphitization catalyst by enabling the dissolution–precipitation formation mechanism of graphite. The initial interaction of carbon with nickel leads to the formation of either solid solutions or nickel carbide, a metastable phase [6]. Depending on the target size and morphology of the graphite product, different configurations of the Ni/C interface are used in conducting the graphitization process. In order to produce graphene structures, nickel films are used as substrates [5]. Graphite-encapsulated nickel nanoparticles can be obtained in the mechanically milled and annealed mixtures of nickel and soot powders [4]. Although the graphitization process of amorphous carbon has been described for various relative contents of the phases and configurations of the Ni/C interface, the aspects of sintering of graphite grains in nickel–graphite composites thus obtained have been rather scarcely addressed. Of particular interest are composites containing comparable volume contents of the phases, which can form continuous networks. Such composites can be fabricated by solid-state consolidation of powders [7], whose structure has been tailored in a way that facilitates the formation of networks of the phases by inter-particle necking and sintering during consolidation. One of the directions of the microstructural design of these composites can be based on varying the length scale, on which the networks of the phases interpenetrate each other.

The connectivity of the networks can be studied by selectively dissolving one of the phases to reveal the network formed by the other phase. Selective removal of copper from the surface of the TiB_2–43 vol% Cu composite pellets of 94–98% relative density consolidated by Spark Plasma Sintering (SPS) and shock compaction resulted in the formation of a porous nano-grained titanium diboride layer that maintained its integrity [7]. The same procedure of selective dissolution of copper applied to conventionally sintered TiB_2–43 vol% Cu compacts, which were only 64% dense, did not allow obtaining a layer adherent to the compact. Similarly, the targeted preparation of porous materials is possible if one of the phases is selectively dissolved [8–11]. Recently, we proposed a novel and simple preparation route of nanoporous silver, which is based on selective dissolution of Fe or Ni from Ag–50 vol% Fe and Ag–50 vol% Ni nanocomposites in the powder state and Spark Plasma Sintered compacts [11]. The nanocomposite structure in

---

* Corresponding author. Fax: +7 383 332 28 47.
E-mail address: dina1807@gmail.com (D.V. Dudina).

http://dx.doi.org/10.1016/j.jpcs.2014.09.007

these composites was achieved by high-energy mechanical milling of the elemental powders. Upon treatment of the Ag–Fe and Ag–Ni nanocomposites in diluted HCl solution, Fe and Ni dissolved revealing a nanoporous silver skeleton.

In the present work, the chemical composition of the system has been selected such that a network could be built by the grains of a phase that forms *in situ* during sintering. The grains of a phase forming *in situ* are more likely to sinter efficiently between themselves during the process compared to the particles introduced *ex situ* into the mixture, in which no chemical transformation occurs. The goal of this study was to evaluate a possibility of producing porous self-supporting graphite structures by forming graphite through *in situ* graphitization during the SPS of nickel–amorphous carbon powder mixtures. In order to obtain porous graphite, nickel was dissolved from the compacts by treating them in HCl solution.

2. Experimental

Carbonyl nickel (99.9% purity, Norilsk Nickel, Russia) and amorphous carbon (95% purity, carbon black PM-15, Omsk, Russia, globule size 100–200 nm) powders were taken as raw materials. The powder of carbon black was annealed in vacuum at 800 °C to remove the volatile contaminants. Transmission Electron Microscopy (TEM) characterization of the particles of amorphous carbon used in this study can be found in Ref. [4]. In order to achieve comparable volume contents of the phases in the composite in the consolidated state, Ni–C mixtures containing 81.3 wt% of Ni were prepared to form 50 vol% Ni–50 vol% C sintered specimens. The mixture was mechanically milled in a high-energy planetary ball mill with water-cooled vials. The powder mixtures were loaded in the milling vials in a glove box under an atmosphere of high-purity argon. The ball to powder weight ratio was 20:1. Stainless steel vials and balls were used. No process control agent was added during milling of the mixture. The milling time was 10 min. For comparative experiments, a Ni–C mixture of the same composition was prepared by mixing the powders in a mortar followed by mixing in a horizontal ball mill.

Spark Plasma Sintering of the powders was carried out using a SPS Labox 1575 apparatus (Japan). Graphite dies of 10 and 20 mm internal diameter and graphite punches were used. The die wall was lined with a carbon foil. Circles of carbon foil were placed between the sample and the punches. The temperature during the SPS was controlled by a pyrometer focused on the die wall for the samples sintered at the maximum temperatures of 700–1000 °C and by a K-type thermocouple NSF600 (CHINO) 1.6 mm in diameter placed in the die wall at a depth of 5 mm for the samples sintered at 500 and 600 °C. The difference between the measured temperature and the actual temperature of the sample in the die was, therefore, higher for the samples sintered at 700–1000 °C (the estimated temperature difference for these samples is 100–150 °C). These temperature measurement methods suited the needs of the present study. The samples were heated at an average rate of 60 °C min^{-1}. The sample was held at the maximum temperature for 10 min and then cooled down to room temperature. At the beginning of the process, a uniaxial pressure of 40 MPa was applied and kept constant through the sintering cycle.

Selective dissolution of nickel from the sintered compacts was performed in 10 wt% HCl aqueous solution. The compacts were placed in the solution for 48 h, removed, washed in deionized water and dried.

The X-ray diffraction (XRD) patterns of the powders and sintered specimens were recorded using a D8 ADVANCE diffractometer (Bruker AXS) with Cu Kα radiation. Using Rietveld analysis of the XRD patterns with TOPAS 4.2 software (Bruker AXS), the lattice parameters were determined and the graphite content in the sintered compacts was estimated.

The microstructure of the powder mixtures, sintered compacts and porous carbon was studied by Scanning Electron Microscopy (SEM) using a Hitachi-Tabletop TM-1000 and a Hitachi-3400S Scanning Electron Microscopes. Secondary electron (SE) and backscattered electron (BSE) imaging modes were used. Fracture surfaces of the compacts were studied.

Specific surface measurements of the porous graphite were conducted using thermal desorption of argon by Brunauer–Emmett–Teller (BET) method.

A model experiment has been performed to study the crystalline and grain structure of graphite formed from an amorphous carbon film deposited on the surface of a Ni foil. The amorphous carbon film was deposited on a Ni foil using an arc discharge between graphite electrodes. The Ni foil coated with amorphous

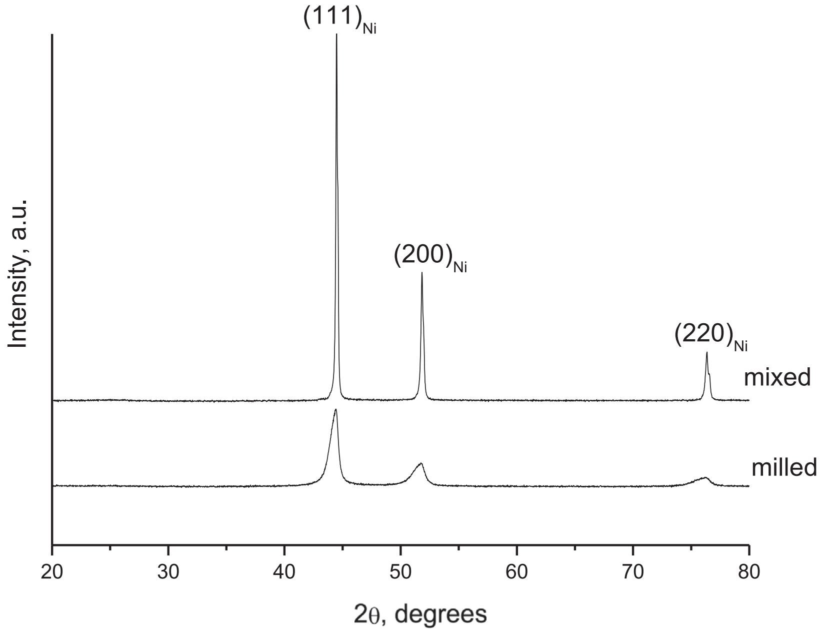


Fig. 1. XRD patterns of the Ni–C mechanically milled and mixed powders.