



Diamond synthesis in aluminum matrix in molten alkali-halide at ambient pressure

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ABSTRACT

The interaction of the molten aluminum with the carbon-containing admixture in a molten halide-alkali medium at atmospheric pressure with temperatures of 700–800 °C under strong non-equilibrium conditions is studied. Cubic diamond crystals of 2–100 μm and nanorods of 20–100 nm diameter and 5 μm lengths are first found forming inside the aluminum matrix under certain cooling regimes. The X-ray diffraction analysis, electron backscatter diffraction spectroscopy, electronic microscopy, Raman spectroscopy and microhardness detection register the perfect cubic diamond formation inside aluminum without applying of high temperature and high-pressure. Diamond formation mechanism is growing by carbon atom diffusion through an aluminum droplet. Diamond and nanodiamond synthesis conducted directly at the carbon ion interaction with the molten metal volume and subsequent cooling regimes.

Prime novelty statement: Diamond synthesis has been performed in molten aluminium via the interaction between molten aluminium and carbide-containing halide melt at 700–750 °C with ambient pressure.

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1. Introduction

The synthesis of artificial diamonds is an important practical and fundamental task in the inorganic synthesis field. The most practically used high-temperature–high-pressure method (HTHP-method) of diamond synthesis was similar to the conditions needed for natural diamond growth. This method was based on the fundamental paper by Soviet scientist O.I. Leypunskii in 1939 [1] where the conditions required for artificial diamond production were formulated, i.e., combination of medium, pressure and temperature.

Nowadays, the primary industrial diamond synthesis method is a solution–melt metal–carbon synthesis at high pressures (temperatures of 1400–1600 °C, pressures of 50–60 GPa) [2–5]. Graphite, or other carbon-containing compounds, and metals or iron, nickel, cobalt, platinum or palladium alloys are typically used as a load. High-pressure chamber hydraulic presses produce the necessary pressure and temperature conditions.

Since the middle of the 1950s, the possibility was shown of growing diamonds using a wide variety of chemical vapor deposition (CVD) techniques [6–11]. Chemical vapor deposition (CVD) involves a series

of gas phases and surface chemical reactions, along with the deposition of reaction products, i.e., diamond, on a solid substrate surface. Unlike HPHT synthesis diamond CVD is usually done at a fraction of 1 atm.

Despite the probability of the diamond crystal nucleation that is less than the graphite nucleation one, it still exists. The energetic advantage of diamond in comparison with graphite caused by the small particle sizes was established by modeling and computation of free energy in Refs. [12–15]. The results, obtained for low external pressure, $P > 0$, and for temperatures up to 1100 °C, indicate that diamond is the stable modification of carbon, and graphite is the metastable one at small particle sizes which are less than the boundary of stability regions of these phases. The intersection of size dependences of free energies of diamond and graphite indicates the size-related stabilization of diamond nanoparticles. The established boundaries of the stability regions of diamond and graphite are 10.2 nm at room temperature, 6.1 nm at 525 °C, 4.8 nm at 800 °C, and 4.3 nm at 1100 °C [13].

If prevent graphite formation, then diamond crystals might nucleate and grow. The carbon atoms melted in metal, and the other carbon compounds, such as carbides, including the metastable ones, functioned as carbon carriers to the growing diamond. The metal or alloys used at the diamond's synthesis are conventionally assumed to provide a good wetting of diamond and graphite in order to dissolve carbon and to have low melting temperatures. The intermediate metal solvent carbides formation was described as the factor that facilitates cubic

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diamonds formation [16]. Otherwise, the synthesis temperature and the applied pressure would be high. Despite the discussion about the importance of intermediate carbides formation, its role in diamond synthesis is not so obvious.

The type of the carbon material and its pore sizes greatly affect the synthesis rate and diamond yield at single-press sintering. In carbon-graphite materials, researcher V.I. Kasatochkin [17] demonstrated that the graphitizing ability of carbon materials (i.e., their ability to form the structure characteristic for graphite) influences their transformation into diamonds. In use, the graphitizing raw material the synthesis terminated faster and the diamond yield was larger than it was in cases where the non-graphitizing carbon material used.

Over the past 10–15 years, numerous investigations involving the production of carbon coatings or nanomaterials, including nanotubes, in molten salt media [18,19] were published. The basic methods of the synthesis of different carbon structures include electrolysis of carbon (graphite) electrodes in molten salts, particularly lithium chloride [19–21], and cathode reduction of carbonate ions or carbon dioxide in molten chlorides, carbonates or fluorides of alkali metals [22–27]. Nevertheless, no diamonds were obtained by these methods using alkali halides media.

The present work studies the direct one-step diamond synthesis in a molten aluminum matrix, using a molten alkali halide medium under atmospheric pressure.

2. Experiment

The interaction between the molten aluminum and the carbon-containing component was performed in molten alkali halides media using an alumina crucible. The carbide powders of either metals or non-metals such as WC, TiC, ZrC, Mo₂C, SiC and B₄C were used as the carbon-containing additive. Carbides with the NaCl structure (e.g., TiC, ZrC) or wurtzite/zinc blend structure (β-SiC) so as rhombohedral B₄C or orthorhombic Mo₂C can be applied as diamond precursors.

Salt mixtures of alkali chlorides and/or fluorides such as LiCl, NaCl, KCl, CsCl, NaF, AlF₃, and NH₄F with melting point under 700 °C were used as base electrolyte. A pre-melted salt electrolyte was thoroughly mixed with specific amount (not more than 10 wt.% of total weight) of carbide powder that had an average grain size of 100–200 μm. The mixture of alkali-halide metals with the carbide addition was placed in the bottom of the crucible. The aluminum sample with 0.1 wt.% impurities (0.009 wt.% Mg, 0.07 wt.% Fe, 3 · 10⁻³ wt.% Mn, 8 · 10⁻³ wt.% Si) represents either a disk that is 5 cm in diameter or grit with the grain size of 3–5 mm.

The aluminum was loaded into part of the salt mixture on the bottom of the crucible. The mixture of alkali-halide metals with the carbide addition also put on the top of the aluminum in order to eliminate the molten aluminum oxidation by oxygen from the air. The alumina crucible was covered with a cap and then placed into the vertical heating furnace to heat to the required temperature. The main experiments were performed at the temperatures of 700 and 750 °C. The interaction temperature was chosen under molten point both the aluminum and the salt mixture. The dwelling time varied from 0.5 to 5 h. After the high temperature exposure, the liquid aluminum globule was poured into the cold alumina crucible. The conditions of the diamond seeds' formation in the aluminum matrix primarily depended on the conditions of the carbon's introduction to the aluminum matrix, as well as further non-equilibrium regime cooling and additional thermal processing.

After the salt mixture froze hard, it was dissolved and the salts were washed off the aluminum globule surface. Then aluminum was cut into two halves. The first half was poured by current-carrying gum and was then polished by six different silicon solutions using the "Struers" disk-finishing machine (Austria). Then the specimen was studied by scanning electron microscopy (SEM) using the JEOL 5900LV and Zeiss Σigma VP microscopes, by Raman spectroscopy, using the "Renishaw-1000" Raman microscope-spectrometer with a green 514 nm argon laser, by optic profilometer-profilograph NYKO NT 1100 by "Weeco"

Table 1
Gibbs energies of possible diamond synthesis reactions.

| Reaction | 700 °C | 750 °C | 800 °C |
|--|-----------|-----------|-----------|
| 4Al + TiC + 4O ₂ = 2Al ₂ O ₃ + C + TiO ₂ (1) | -1946.576 | -1915.880 | -1885.511 |
| 4Al + WC + 3O ₂ = 2Al ₂ O ₃ + C + W (2) | -3333.713 | -3292.155 | -3250.668 |
| 4Al + B ₄ C + 6O ₂ + 12NaCl = 2Al ₂ O ₃ + C + 4BCl ₃ + 6Na ₂ O (3) | -2703.960 | -2670.820 | -2637.724 |

in Vertical Scanning Interferometry (VSI) regime, by microhardness tester VMHT AUToman (Leica Microsystems), and the optic microscope "Neophot 32". Electron backscatter diffraction (EBSD) patterns were obtained using HKL NORDLYSS console software Channel 5.

Another part of the aluminum was dissolved in a 20 wt.% HCl solution, and then fine transparent crystals were deposited on the titanium foil substrate for further analysis. The transparent crystals deposited on the titanium foil were photographed by SEM microscope and then were analyzed by grazing-incidence X-ray diffraction (Rigaku DMAX 2200PC) and by Raman spectroscopy (Renishaw).

3. Results and discussion

The study of interaction of carbide powders with molten aluminum in the molten alkali chloride-fluoride mixture has been carried out under air in the temperature range of 700–800 °C. Having the melting point over 2500 °C, titanium carbide, boron carbide and tungsten carbide, for example, are ones of the most thermodynamically stable compounds. There is no direct decomposition of carbides into constituents with carbon formation at given temperature range. The calculations of

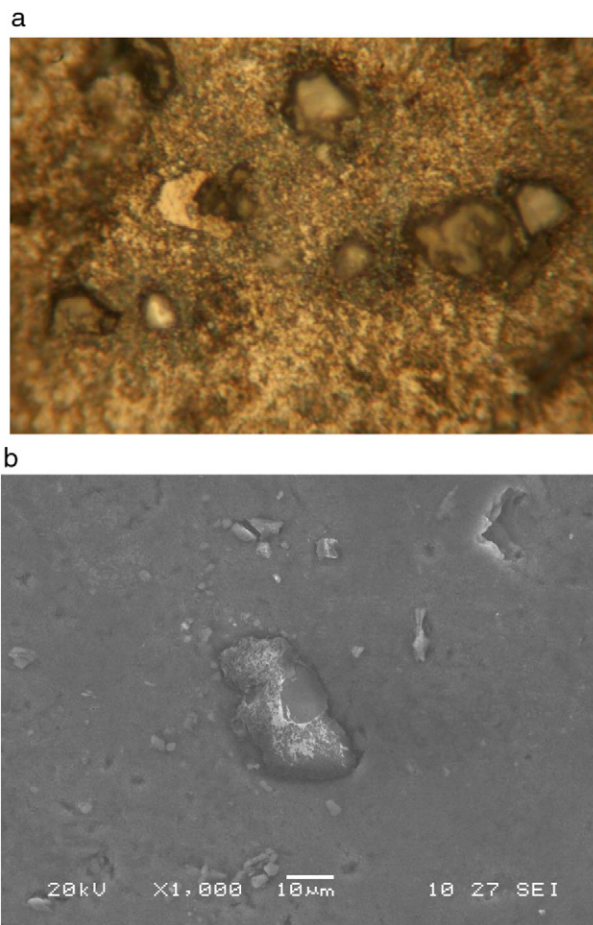


Fig. 1. (a) Optic image (×100), (b) SEM image of carbon inclusions in aluminum cross-section.

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