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Interaction of Diamond with Ultrafine Fe Powders Prepared by Different Procedures

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Abstract—We have studied the interaction of synthetic diamond crystals with ultrafine Fe powders during catalytic diamond gasification in a hydrogen atmosphere at 900°C. The Fe powders were prepared by three procedures: reduction of Fe_2O_3 nanopowder; evaporation using an ELV-6 electron accelerator, followed by condensation; and reduction of ferric chloride. The surface-processed diamond crystals were examined by electron microscopy. The results indicate that ultrafine powders produced by the first two procedures cause predominantly lateral etching of diamond. The Fe particles prepared by the third procedure penetrate into the bulk of diamond crystals and produce etch pits and "tunnels," thereby markedly increasing the specific surface area of the crystals.

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INTRODUCTION

Thermochemical (nonabrasive) processing of synthetic and natural diamond is a chemical process because it relies on catalytic diamond gasification in a hydrogen atmosphere [1]. This process involves four steps:

(1) transfer of carbon atoms from diamond to the surface layer of the metal catalyst,

(2) carbon diffusion in the bulk of the metal,

(3) vaporization of the carbon dissolved in the metal, and

(4) the removal of the gaseous carbon-containing species from the reaction zone.

Several techniques for diamond processing are based on this process: marking (including engraving), cutting, deep pattern etching, lapping, polishing, and brazing of metallic contacts to diamond [2]. In the last case, a microscopically rough diamond surface is needed [3].

There is solid experimental evidence that, when powder catalysts are used, etching with transition metal particles depends on the crystallographic orientation of the face and the structure of the diamond crystals [4, 5]. This effect is particularly highlighted by comparison of synthetic and natural diamond crystals. This is caused by the presence of defects, around which interaction mainly occurs. Synthetic diamond crystals grown under stable conditions are more perfect than natural diamond. For this reason, they are etched for the most part laterally (along their faces), whereas natural diamond is etched along the normal to its faces, with the formation of very rough surfaces. Such studies were carried out for metal particles ranging in size from 1 to 3 μm.

This work examines the interaction of diamond with smaller Fe particles (100 nm or less in size) prepared by different procedures with the aim of studying the etching behavior of diamond in the course of hydrogenolysis.

EXPERIMENTAL

Experiments were carried out in flowing hydrogen in a water-cooled temperature-controlled microchamber equipped with an observation window. The process was followed using an MBS-9 optical microscope. Hydrogen was produced by an SGS-2 electrolytic generator and was introduced into the microchamber at a flow rate of 3 l/h. The temperature was measured by a W/Re thermocouple. The investigation technique was similar to that described elsewhere [6, 7].

We studied diamond crystals grown on (001)-oriented seeds in the Fe–Ni–C system at 5.5 GPa and 1500°C using a split-sphere multianvil high-pressure apparatus and a procedure described earlier [8]. The crystals had octahedral habits with cube and trapezohedron modifying facets and belonged to type Iba according to the physical classification.

The catalyst used was ultrafine Fe powder, which offers the highest catalytic activity for the process in question [9, 10]. Fe particles suspended in a drop of ethanol or BF-6 adhesive diluted with ethanol were applied to {111} faces of diamond crystals cleaned with a mixture of $K_2Cr_2O_7$, H_2SO_4, HCl, and H_2O and dried. After ethanol evaporation, the crystals were placed in the microchamber.

Ultrafine Fe powders were prepared by different procedures.

In one procedure, ferric oxide (Fe_2O_3) powder (OSCh 2-4 grade, Donetsk Plant of Chemical Reagents) was reduced directly in the microchamber during heating. The particle size ranged from 100 to 300 nm as determined by electron microscopy. The ferric oxide particles formed spherical agglomerates up to 10 μm in size.

In another procedure, Fe powder was prepared using an experimental setup built around an ELV-6 commercial electron accelerator (Budker Institute of Nuclear Physics, Siberian Branch, Russian Academy of Sciences).

The setup for the preparation of metal nanoparticles comprised the ELV-6 accelerator, an evaporator reactor, a condenser, and a filtration system (Fig. 1). The accelerator parameters are as follows: electron energies from 0.8 to 1.5 MeV; beam power, up to 100 kW; and beam current, up to 100 mA. In our experiments, the accelerator parameters were as follows: electron energy, 1.4 MeV; beam current, 3 mA; and beam power, 4.2 kW. To produce nanoparticles in this setup, a metal is heated by an electron beam to boiling in the evaporator reactor and evaporated. The vapor is then cooled in a flowing inert gas (argon) in the condenser. This procedure ensures an almost inertialess energy transfer to a substance, with keyhole melting and effective evaporation of the metal. The Fe particles obtained using the ELV-6 accelerator ranged in size from 100 to 300 nm.

In addition, to minimize Fe particle agglomeration we attempted to deposit particles onto the surface of diamond crystals directly in the setup. Several diamond crystals were glued with BF-6 in different parts of the setup: on the lateral, cylindrical surface and lid of the condenser, on the lateral surface and bottom of the container in the filtration system, and in the outlet pipe downstream of the filter. To study the deposited particles, a special film was glued in the condenser.

In that experiment, no inert gas was used because we wanted to obtain iron oxide particles. This was done because iron oxide particles crystallizing from the vapor phase were faceted and were expected to acquire an active surface during hydrogen reduction.

The resultant particles ranged in size from 20 to 100 nm (Fig. 2). The experiment was performed at an electron energy of 1.4 MeV (Fig. 3).

In a third procedure, $FeCl_3 \cdot 6H_2O$ (pure grade, RF State Standard GOST 4147-74) in solution (1 or 5 g of ferric chloride for 100 ml of water) was used as the precursor to ultrafine Fe particles. A drop of the solution was placed on the surface of a diamond crystal. After drying, the crystal was placed in the microchamber, where the ferric chloride was reduced to metallic Fe in hydrogen.

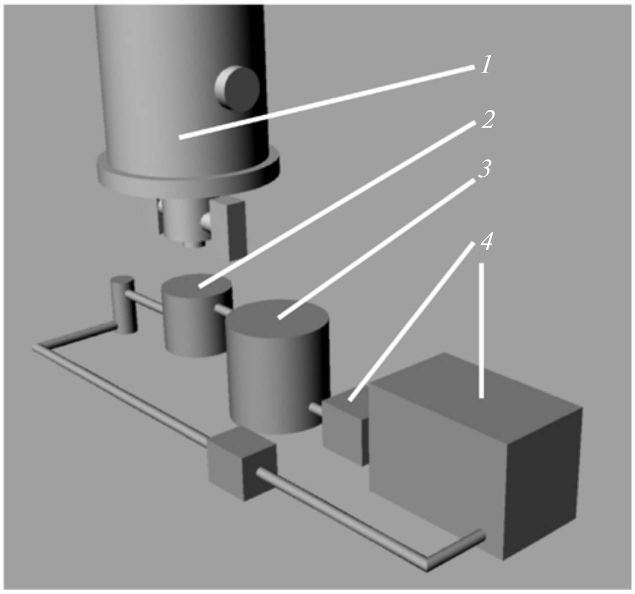

Fig. 1. Schematic of the experimental setup for the preparation of metal nanoparticles using an ELV-6 accelerator: (*1*) ELV-6 electron accelerator, (*2*) evaporator reactor, (*3*) condenser, (*4*) filtration system.

All experiments were performed under standard conditions: 900°C, 1 h (one experiment took 15 min; the crystals were then examined under an MBI-15 optical microscope and again heated). Next, the surface of the diamond crystals was examined on an LEO 1430 electron microscope.

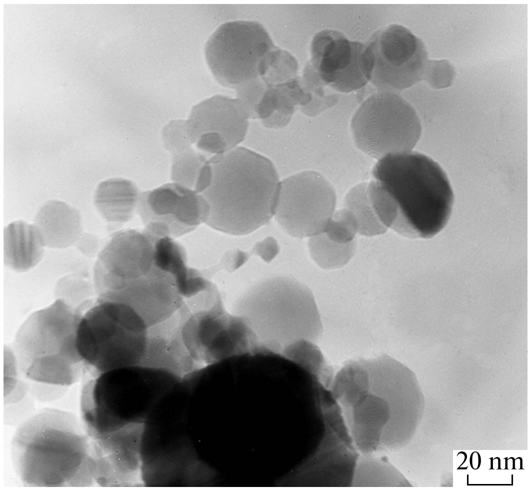

Fig. 2. Iron oxide particles deposited on film in the condenser of the setup at the ELV-6 accelerator.

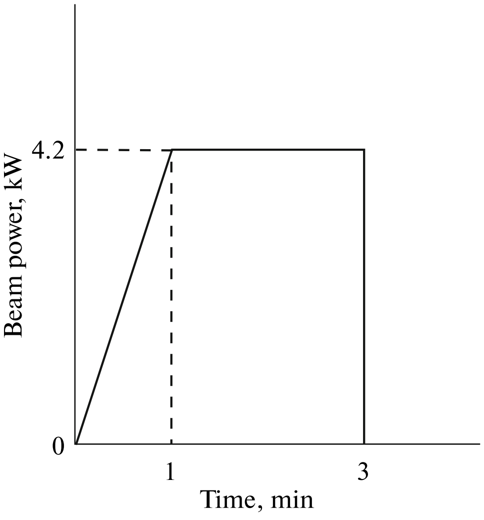

Fig. 3. Accelerator current vs. time in an experiment aimed at depositing iron oxide particles onto diamond crystals.

RESULTS AND DISCUSSION

The interaction of diamond with Fe particles prepared by reducing OSCh 2-4 Fe_2O_3 or using the ELV-6 electron accelerator produced complex etch patterns in the form of numerous grooves on the octahedron faces of synthetic diamond crystals in hydrogen (Fig. 4). The etch patterns are traces of Fe particles migrating over the diamond surface. Their width corresponds to the size of the Fe particles. Some of the grooves have a flat bottom parallel to the (111) plane. There are few or no straight grooves: they are typically tortuous, with many irregular bends. From a local area of a face, Fe particles may migrate in various directions, even in opposite directions. The grooves intersect at various angles. The behavior of Fe particles in an already existing groove is also irregular: they may move in the same direction as the preceding particle, intersect its trace, or move in the opposite direction.

One drawback to this process is particle agglomeration. Agglomerated particles make broad, striated grooves where an individual stria corresponds to an individual particle. Large agglomerates of Fe particles typically move in one direction and rarely change the direction of their motion. In addition, the Fe particles have faceting elements in the form of small flat facets.

As expected, the number of particles deposited onto the surface of diamond crystals using the electron accelerator was very small and had a local distribution. Most of the particles were not agglomerated and ranged widely in size. The number of particles on the crystals situated in the container of the filtration system exceeded that on the crystals in the condenser. Nevertheless, the interaction of Fe particles with the surface of diamond crystals was similar to that in the experiments described above (Fig. 5). The size of the etch grooves was minimal across the samples. The corresponding size of the Fe particles was ~50 nm.

Thus, the key features of the interaction of the ultrafine Fe particles prepared using the ELV-6 electron accelerator and by reducing Fe_2O_3 with the octahedron faces of synthetic diamond crystals in a hydrogen atmosphere are predominantly lateral etching and random migration of the particles over the octahedron faces. This is in full accord with earlier results for micron-sized Fe particles [5, 6].

The results obtained by reducing $FeCl_3$ differed drastically from those above. There was little or no lateral etching, i.e., no migration of Fe particles over the surface of diamond crystals and no etch grooves. The Fe particles produced by hydrogen reduction rapidly penetrated into the bulk of the crystals and produced etch pits and “tunnels” (Fig. 6). The individual pits ranged in size from ~200–300 to 50 nm or, possibly, less. These values are the sizes of the Fe particles.

Thus, when ultrafine Fe particles are prepared via reduction of ferric chloride, diamond crystals are etched only along the normal to their faces. It is also of great interest that this etching behavior is independent of the crystallographic orientation of diamond crystal

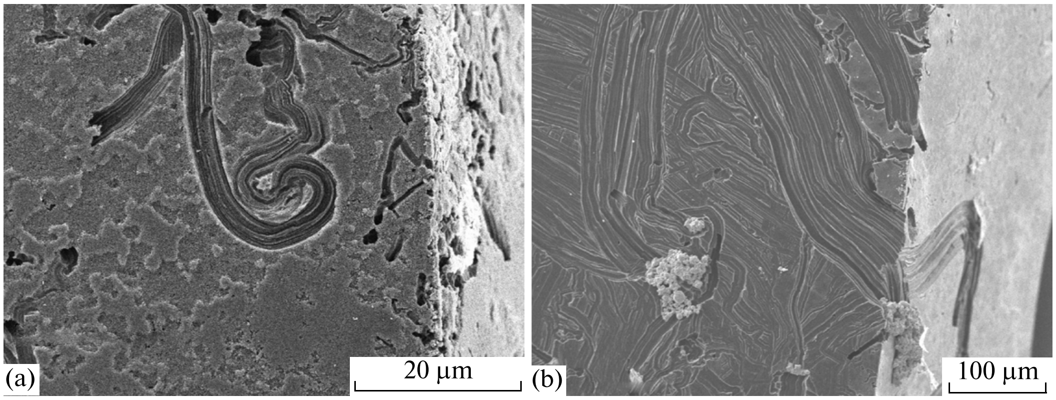

Fig. 4. Typical etch patterns produced on the octahedron faces of diamond crystals by hydrogenolysis catalyzed by Fe particles prepared (a) by reducing Fe_2O_3 and (b) using the ELV-6 electron accelerator.

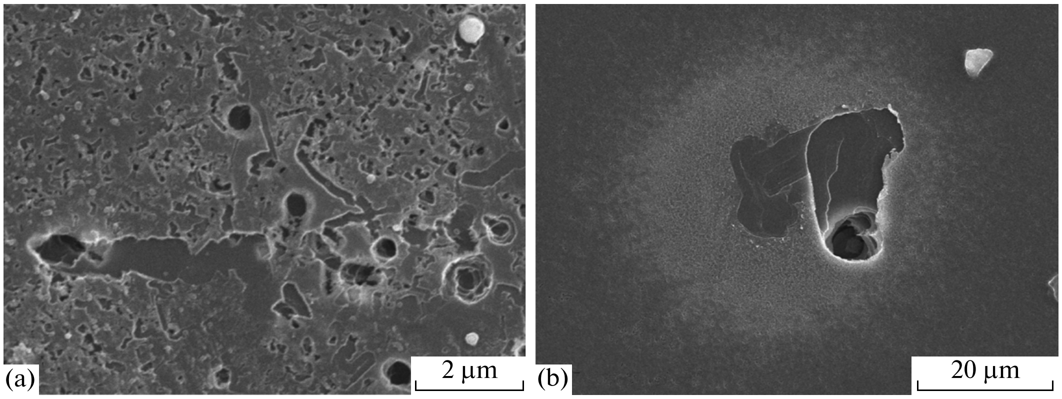

Fig. 5. Etch patterns produced on the octahedron faces of diamond crystals by hydrogenolysis catalyzed by Fe particles prepared by reducing ferric oxide deposited using the ELV-6 electron accelerator. The arrows show the migration direction of a metal particle.

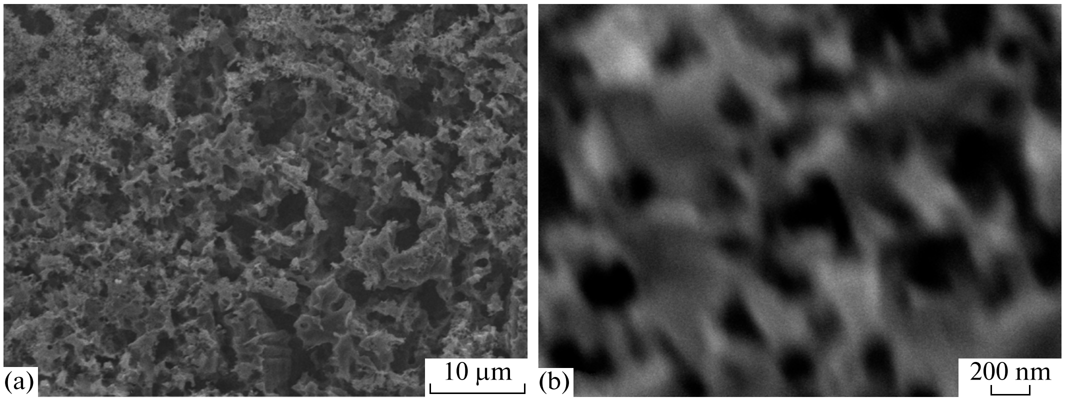

Fig. 6. Etch patterns produced on the octahedron faces of diamond crystals by hydrogenolysis catalyzed by Fe particles prepared by reducing ferric chloride.

faces; i.e., faces differing in Miller indices have similar etch patterns. Such processing produces extremely active diamond surfaces, which suggests that this effect might be used not only to fabricate composite materials with brazed diamond layers and tools containing diamond parts brazed to metallic holders but also to prepare active diamond powder adsorbents for chromatography, diamond whiskers, etc. The described approach is competitive with processes that rely on the oxidation of diamond surfaces [11, 12].

Note that the effect in question requires further investigation because a transition from one rate-limiting steep to another is possible during catalytic diamond hydrogenolysis.

CONCLUSIONS

Using Fe as an example, we have shown that the etching of diamond crystals by ultrafine catalyst particles during hydrogenolysis depends on the particle preparation procedure. One possible reason for this is that the preparation procedure influences the surface activity (degree of faceting) of the particles. Ultrafine powder prepared by reducing ferric chloride markedly increases the specific surface area of diamond crystals, thereby extending the field of their potential applications.

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