

Solid-state reaction of niobium with diamond carbon at high pressure and high temperature to form superconducting composite

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S1. General information and material synthesis

In this research we used commercially available extra purified DNDs (ash content < 0.1 wt.%) from Joint Stock Company “SKTB Tekhnolog” (St.Petersburg, Russia) and pure (99.9%) niobium powder with grain size of 45 μm (#354906) from Kojundo Chemical Laboratory Co., Ltd (Saitama, Japan). The size of DND aggregates consisting of 5-nm diamond crystallites was ~100-200 nm. According to X-ray photoelectron spectroscopy (XPS), the surface oxygen content in the precursor DND was 8.2 at%.^{S1} Perkin-Elmer PHI 5600 Multi-Technique XPS system of Hosei University (Tokyo, Japan) with monochromatized Al $K\alpha$ radiation was used for this characterization.

XRD patterns were recorded with Rigaku Smartlab III X-ray diffractometer in Bragg-Brentano geometry. Radiation source: $\text{MoK}\alpha$, $\lambda=0.7093\text{\AA}$. In this case, several uneven pieces of the fractured composite were simultaneously placed on a glass cell for powder measurements. For identification of the NbC phase, the diffraction pattern of mineral niobocarbide calculated by EXPO from COD database CIF file data was used. Card COD ID 900-8682. <http://www.crystallography.net/cod/9008682.html>.^{S2}

Commercial DND powder was purified in boiling 35% hydrochloric acid (4-5 times) and thereafter washed in boiling distilled deionized water (4-5 times) for removal iron, iron-related complexes and other 3d-ferromagnetic impurities. The dense sedimented part of DND suspension was thereafter dried in secondary vacuum at 110 °C. The details of such procedure were described earlier.^{S3} The obtained powder of grey colour was mixed with a certain amount of niobium 45- μm powder in an agate mortar until reaching the homogenous mixture. The prepared Nb/DND mixture is then transferred to an inner graphite cylinder of a toroidal type high-pressure chamber for sintering. Typical dimensions for an internal hollow graphite cylinder were i.d. 4.0 mm, height 5.5 mm. This hollow cylinder was closed on both sides by graphite lids. The mixture was heated by rapid heating of a graphite cylinder with a direct current after a high pressure of 7 GPa was applied. About ~250 mg of precursor Nb/DND mixture was treated during one press run. Sintering took place under high pressure and high temperature conditions (from 1330°C to 1990 °C) for 60

seconds in such a press. As a result of sintering, after the subsequent removal of the walls of the deformed graphite cylinder, a dark solid pellet was obtained. The dark colour of the tablet is due to contact with a graphite heater during sintering and excess carbon in the near-surface layers of the composite. When such a tablet was broken into two approximately equal halves, a shiny metal fracture surface was found. The two halves of this broken tablet (sample Nb26) are shown in Figure S1.

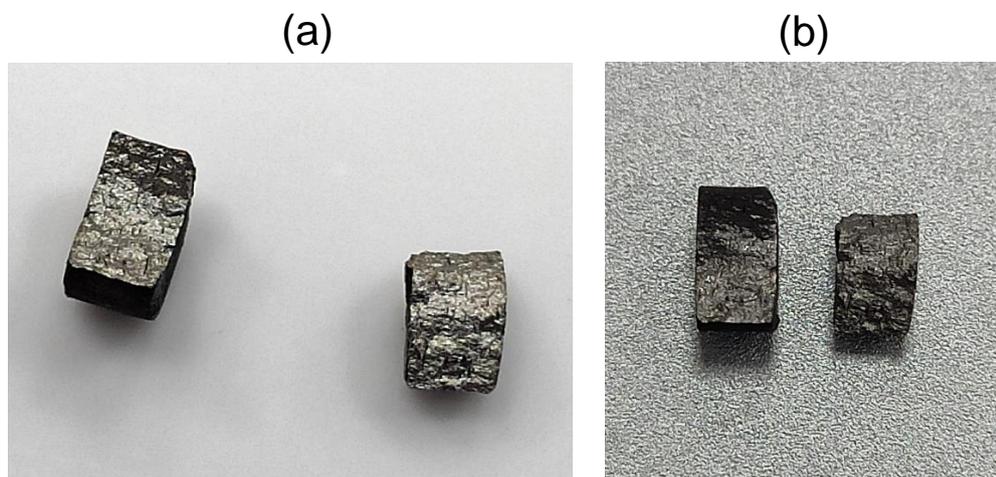


Figure S1 Optical images of two halves of a Nb26 composite tablet split in half, prepared from 90 wt% niobium and 10 wt% DND. A metallic luster is clearly visible on the fault surface. The images are given against the background of a sheet of white plastic (a) and against the background of the surface of an Al-Mg alloy with a specially unpolished surface (b). Tablet diameter - 4 mm.

S2. Electron microscopy and elemental analysis data

The morphology of the fracture surface of the Nb26 composite was studied using a JEOL JSM-6390 scanning electron microscope (Japan) with the ultimate resolution of 3 nm. The images of the fractured surface were obtained at 15-20 kV accelerating voltage. The elemental composition of the selected areas from the sample surface was determined using an energy-dispersive X-ray spectroscopy device Oxford INCA Energy EDS (England). When studying the elemental composition, an accelerating voltage of 10 kV was used, and the selected rectangular regions in the SEM image of the sample were irradiated with an electron beam. In this case, the EDS detector analyzes the spectrum of characteristic X-rays emerging from these rectangular areas and assigns each of the spectrum components to one or another chemical element.

Several electron microscopic images of the cleaved surface of the Nb26 sample are shown in Figure S2. Carbon inclusions several tens and even hundreds of microns in size are clearly visible (Figure S2, right column), as well as micron crystallites of NbC and Nb at high magnification (Figure S2, left column). The elemental composition of crystallites from the surface areas shown in Figure S2 (a,b) is close to the stoichiometric NbC. The interface between carbon inclusions and niobium carbide is, in most cases, sharp, and the carbon inclusions themselves, as can be seen from Figure S2(c,d), are graphitized. The reason for the appearance of carbon inclusions in the composite of almost stoichiometric composition will be the subject of a separate consideration in subsequent articles.

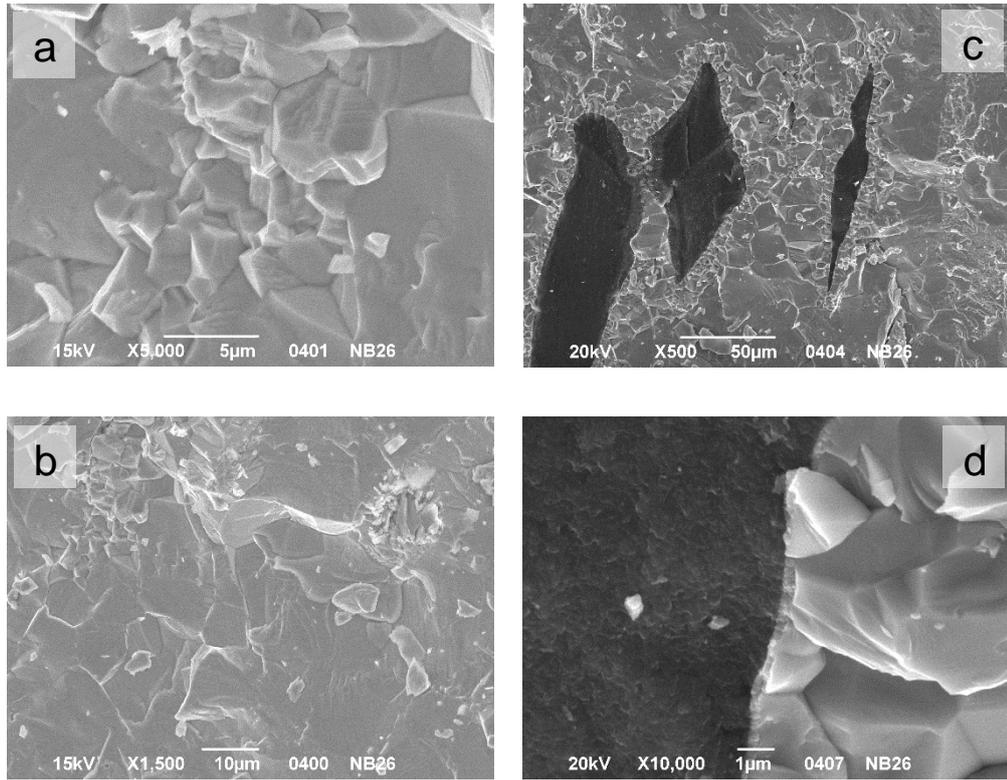


Figure S2 Electron microscopic images of some areas from a cleavage of the Nb26 composite showing individual NbC and Nb crystallites (a, b), carbon inclusions (c), and the interface between the NbC and C phases (d). Black areas correspond to graphite. Bars, μm : a - 5, b - 10, c - 50, d - 1.

S3. Low temperature magnetization curve data

Magnetic measurements were carried out using an MPMS-7 SQUID magnetometer manufactured by Quantum Design (US). A sample in the form of a cylindrical tablet weighing approximately 231 mg was placed in the center of a plastic tube (straw) and fixed tightly there. Before measurements, a straw with a sample inside, fixed on a rod in the measuring chamber, was repeatedly ventilated with helium vapor at $T = 380 \text{ K}$ to remove air adsorbed on the sample. The temperature dependence of the magnetic susceptibility of the sample in the range of 2-300 K was measured in a magnetic field of 250 Oe, and the magnetization curve of the sample in the range from zero to 7000 Oe at a temperature of 2 K. Measurements of the temperature dependence of the magnetic moment began at a temperature of 2 K, after preliminary cooling of the sample from room temperature to 2 K in zero magnetic field and applying a weak magnetic field (less than H_{C1}) to the sample. In the course of measurements, the specified temperature was maintained with an accuracy of 0.02 K, and the measurements of the magnetic moment began only 60 s after the temperature and/or magnetic field had stabilized. The magnetic moment (M) was determined after the completion of three programmable vertical scans of the sample in the SQUID detector chamber (two counter-connected turns of the superconducting wire) and averaging the scan results. The magnetic susceptibility (χ) was defined nominally as the ratio of the specific magnetic moment of

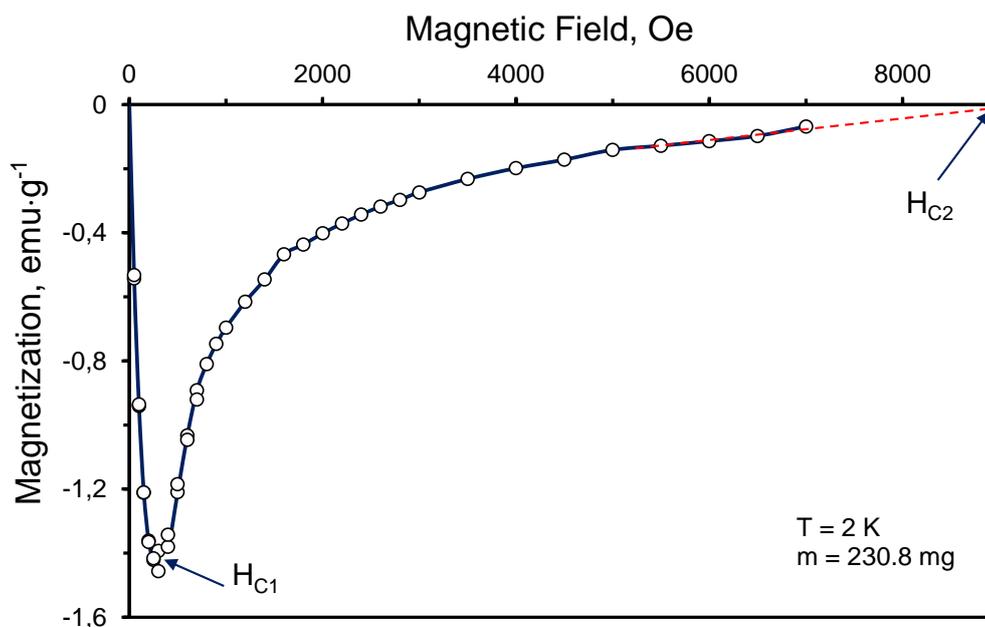


Figure S3 The magnetization curve of the Nb26 sample, recorded at a temperature of $T = 2$ K using a SQUID magnetometer. The critical magnetic fields corresponding to the magnetization curve of such a type II superconductor are approximately ~ 300 Oe and ~ 8900 Oe.

the sample (M/m) to the magnetic field (H) specified in gauss or oersted units.^{S4} Here M and m are the magnetic moment and mass of the sample, and H is the applied magnetic field.

The magnetization curve of the Nb26 sample recorded at 2 K is shown in Figure S3. This shape of the curve corresponds to the characteristic of a type II superconductor with critical magnetic fields H_{C1} and H_{C2} . In a H_{C2} field, superconductivity finally disappears and the composite passes from a diamagnetic to a paramagnetic state with a positive value of the magnetic susceptibility. At $T = 2$ K in the range of magnetic fields from 0 to 300 Oe, the material demonstrates the Meissner effect with the pushing out of the magnetic field lines from the bulk of the superconductor. In this case, the diamagnetic susceptibility is maximum negative and close to the theoretical value ($-1/4\pi$) for a classical superconductor.

References

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