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Crystallization of Diamond below 1 atm from Carbon–Metal Mixtures

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We report the result that various forms of solid carbon can be converted, essentially completely, to well crystallized diamond below atmospheric pressure if mixed with small amounts (ca. 1–10 wt.%) of metallic Mo (or Cu or Ni) and heated in a pure H₂ [or H₂–(1%)CH₄] plasma, excited typically in a 2.45 GHz microwave field at 600–1000 °C.

Keywords: Diamond; Carbon

The work of Derjaguin and co-workers^{1–3} laid the groundwork since the fifties for the current worldwide effort on chemical vapour deposition (CVD) diamond-film synthesis research. Their key finding was that in the presence of atomic hydrogen, the sp³ diamond phase is strongly preferred (and hence survives and grows) compared to the sp² bonded graphite, which is volatilized off.

Kamo *et al.* at NIRIM⁴ in Japan were the first to utilize a microwave plasma as a simple means for depositing thin diamond films on a wide variety of substrates. The Penn State MRL first reported the duplication in the US of the Japanese CVD work in a microwave plasma.⁵ Since then an enormous worldwide effort involving a few hundred laboratories is now actively pursuing the science and technology of diamond films. Excellent reviews by DeVries,⁶ Badzian and DeVries,⁷ and Angus⁸ provide appropriate background on the CVD diamond-film status.

The CVD process grows diamond by the pyrolysis of a gaseous carbonaceous species (CH₄, C₂H₂, CH₃OH, *etc.*) through the transport of the carbon atoms over long distances to (slowly) build up thin solid films on various substrates. On the other hand, the older high-pressure process for growing diamonds used solid-state sources and a liquid metallic catalyst, and produced a mass, typically, of 1–5 mm size single crystals.

In parallel research we have reported elsewhere⁹ on this low-pressure solid-state source method which transforms virtually any form of finely divided carbon into diamond by utilizing a (nano)composite precursor made with very fine diamond, Si, or related materials as a 'catalyst'. The three methods are compared in Fig. 1. We have now extended this work by mixing in (usually by sol–gel techniques or ultrasonic mixing) powders of metallic Mo in the 1 μm size range, with finely divided graphite (*e.g.* Aquadag) or amorphous carbon. The Cabot Company's Vulcan carbon, or ordinary charcoal, has also been used. A layer, up to some 10 μm thick, of this composite placed on an Si or Mo substrate was then exposed to a pure H₂ plasma at 90 Torr† in a tubular 2.45 GHz microwave plasma reactor at 950 °C for 4–6 h. Also, a (99%) H₂–(1%)CH₄ gas was sometimes used. Fig. 2 and 3 show the scanning electron microscopy (SEM) and Raman spectra of the resulting material from the run of the sample with Mo. Excellent crystals of diamond are formed. The X-ray diffraction data show a clean diamond pattern in all cases, sometimes mixed with small amounts of the metal or carbide phase. The experiment has been repeated with Ni powder

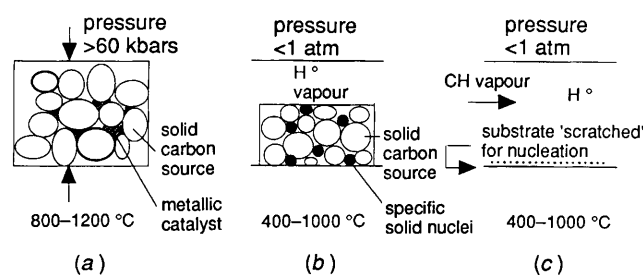


Fig. 1 The three diamond synthesis processes. (a) HPHT SSS: the traditional high-temperature high-pressure process used worldwide for diamond synthesis starts with solid carbon which is transformed to diamond by use of a liquid metal phase as a catalyst. (b) LPSS: the new process, which also uses a pre-shaped solid source consisting of carbon mixed with a very fine second solid phase of isostructural semiconductor or heterotypic metals. The fluid catalyst will involve the H° vapour. (c) CVD: the CVD process utilizes carbon atoms brought into the chamber as a vapour and deposits them on a substrate, often scratched or nucleated with a second phase

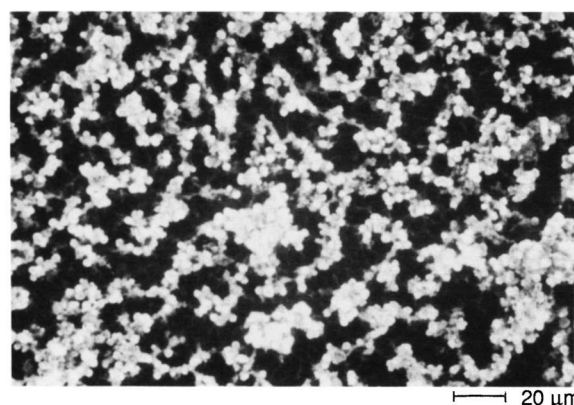


Fig. 2 SEM of Aquadag mixed with 10 wt.% Mo reacted in a hydrogen plasma showing conversion to diamond

which works even better; copper works but not quite as well on a weight percent basis. When we add in both metallic Ni and diamond seeds, we obtain a much denser body of diamond. Similarly, a much denser diamond film is obtained with Ni powder when 1% CH₄ is added to the gas (see Fig. 4), whereas hardly any diamond is formed if no Ni has been added. Various sizes and shapes of the shaped gels from 50 μm up to several mm are converted to diamond partly or wholly depending on the density of the precursor pellets or shapes.

† 1 Torr = 133.322 Pa.

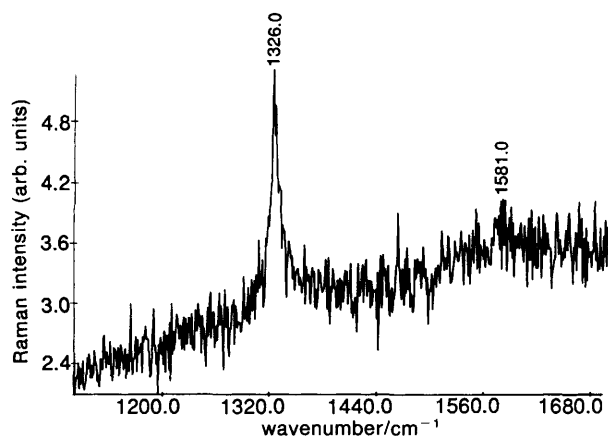


Fig. 3 Raman spectrum of the converted diamond using Mo second phase

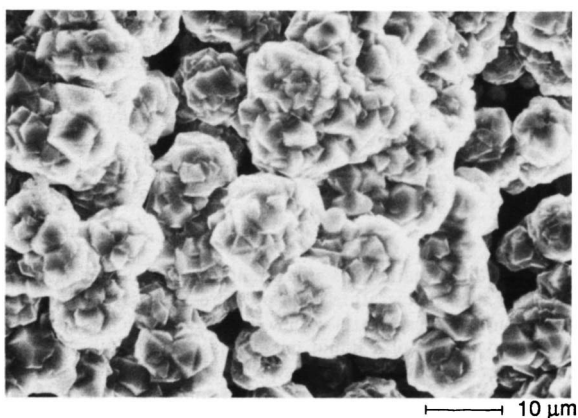


Fig. 4 SEM of processed Aquadag sample with both 10 wt.% Ni and 1 wt.% of <1 μm diamond powder added prior to reaction

Porous diamond bodies in this size range can be made, and subsequently made denser.

To get the optimum conversion, there is a combination of process variables which have to be carefully controlled. Among these are: hydrogen pressure, hydrogen flow rate, material of the sample holder and composition of plasma gas. For example, it has been found that in the case of nickel as the second phase, BN holders produce a very different morphology. Likewise the addition of 1% methane gas increases the size and euhedral nature of the diamond crystals formed, but prevents deeper penetration of the conversion.

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