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Diamond synthesis in graphite/nickel composite powders subjected to shock compression

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Characterization of graphite/nickel composite powders subjected to high-pressure shock-wave compression was performed using optical and transmission electron microscopy. Unique spherulites of graphite were observed in the nickel matrix of those specimens in which the nickel apparently melted under the shock-wave loading. The morphology of these spherulites resembles that of nodular graphite found in cast iron. Evidence of diamond formation was found both at the centre of spherulites (polycrystalline) as well as in the remaining graphite flakes (single crystal).

1. Introduction

In the dynamic synthesis of diamond from graphite/metal mixtures under shock compression, the metal (copper or iron) is said to act as a heat sink to quench shock heating rapidly in order to avoid regraphitization at decreasing pressures [1]. However, as yet the micro-mechanisms of diamond formation under shock compression are not well understood [2]. The most recently proposed model involves a complex solid–vapour–liquid–solid sequence of phase transformations [3]. If this model is substantially correct, the role of a metal may not merely be that of a coolant: it could take part in the synthesis as a chemical agent as well as a physical one. Kleiman *et al.* [3] suggest that catalytic action may promote heterogeneous nucleation of various phases. Another possible influence of metallic additives may be due to the reverberation of dynamic pressures resulting from the impedance mismatch at grain boundaries between metallic and graphite particles.

This paper describes the results of shock recovery experiments with graphite/nickel composite powders. Special emphasis is placed on the characterization of recovered specimens before or without the commonly practiced separation of diamond products by dissolution of the metallic components in acids [3, 4]. Metallographic and transmission electron microscopy (TEM) studies were conducted to gain *in situ* information about the microstructure and, possibly, new perspectives on the synthesis of diamonds under shock compression.

2. Experimental procedure

The nickel-coated graphite powders were commercially manufactured by hydrogen reduction in an aqueous metal salt solution [5]. The nickel content of the powder was 85 wt %. Shock recovery experiments were performed using a mousetrap-type plane-wave generator system [6]. The powders were pressed to 50% to 60% theoretical density in stainless steel capsules measuring 12 mm diameter and 5 mm high. An iron flyer plate was impinged upon the capsules at velocities of 1.1, 1.6 and 2.1 km per sec. The exact loading conditions in the powders are not known but numerical simulation of the recovery fixture using rutile at 55% density impinged at 2.5 km per sec shows peak loading temperatures ranging from 2046 to 4600° C depending on locations [7]. If we scale them, using the dissipated kinetic energies, we find similar peak temperatures for the composite powder at the velocity of 2.1 km per sec and 50% density. These estimates are consistent with the finding that the sample compacted at 1.1 km per sec did not exhibit any sign of bulk melting of the nickel, as did the others. Peak pressures, estimated similarly, were found to be in the range of several tens of giga pascals.

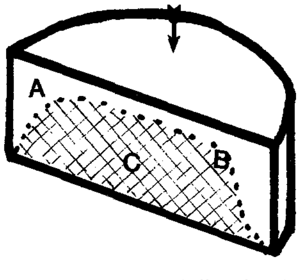

Figure 1 Sketch of shock-compressed disc showing unreacted (A), transition (B) and reacted (C) regions. Arrow indicates direction of shock entry.

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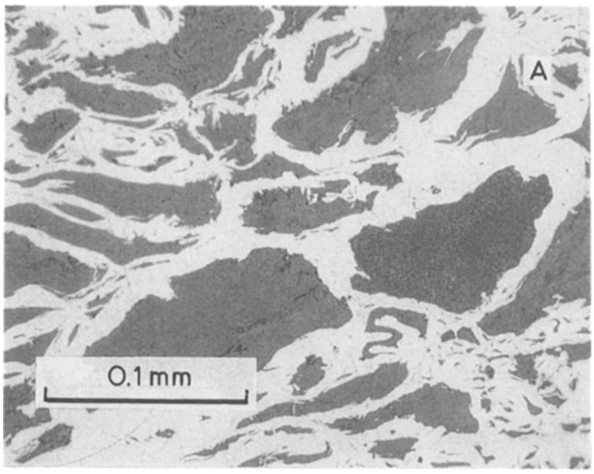

Figure 2 Light micrograph of region A. Graphite flakes are black, the nickel matrix is white.

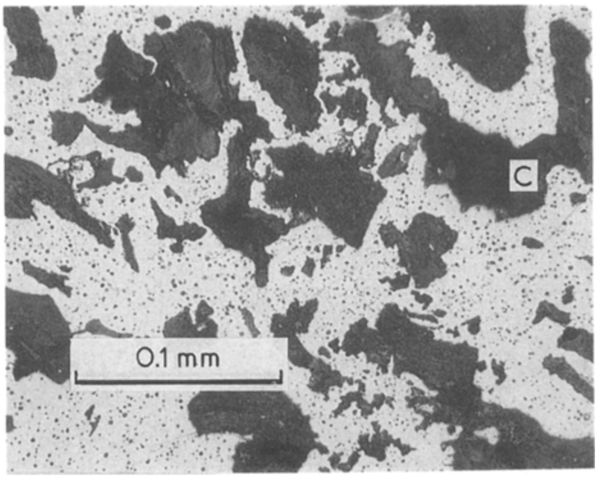

Figure 4 Light micrograph of region C. The graphite flakes are fractured and the nickel matrix is permeated with spherulites.

The most illuminating of the samples from a microstructural point of view was that compacted at 1.6 km per sec. It contained features of both the specimens compacted at the other velocities, and therefore was investigated in depth as representative of the series.

Fig. 1 is a schematic drawing of the disc compacted at 1.6 km per sec indicating the three distinct regions which were noticeable even to the unaided eye along the cross-sectional surface after polishing. A colour change extended from the lower face of the disc towards the top and peripheral surfaces. The top surfaces, as indicated by the arrow in the drawing, experiences the shock entry and, according to simulation experiments [7], has only about half the temperature increase as the material in the bottom region during the compression. However, the crescent-shaped portion of higher temperature was not observed in the simulation. We have no explanation for this discrepancy. In the following, these regions will be referred to as indicated in the drawing: area A "unreacted", area B "transition", area C "reacted".

Specimens for transmission electron microscopy (TEM) were prepared from sections of area C. These were ground and polished to about 40 μm thickness without the use of diamond polishing compounds to avoid any inadvertant introduction of diamond artefacts. Final thinning was accomplished by ion milling.

3. Results

Figs 2 to 4 show optical micrographs of the polished cross-sections of areas A, B and C, respectively. Fig. 2 (area A) shows a well-compacted mixture of nickel and graphite with no obvious signs of the former surfaces of the nickel grains. The graphite flakes have retained their sharp, fibrous morphology. In contrast, the graphite flakes in area C, as shown in Fig. 4, are broken up and the nickel is permeated with spherical black particles. The size of these particles (up to 2 μm diameter) was largest in the zone within the compacted disc which experienced the highest temperature, according to the numerical calculations [7]. Fig. 3, area B, shows a definite border between reacted and unreacted material while the spheres visible here are significantly smaller than in area A. We believe that the features in the "reacted" regions were caused by the melting of the nickel under the high-pressure shock compression.

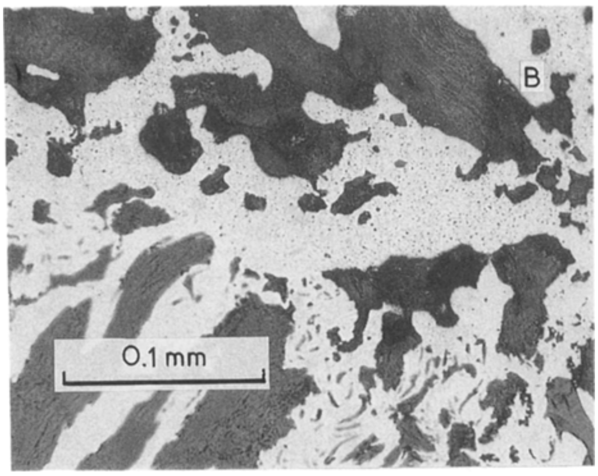

Figure 3 Light micrograph of region B, interface between regions A and C, the latter showing numerous small spherulites dispersed throughout the nickel.

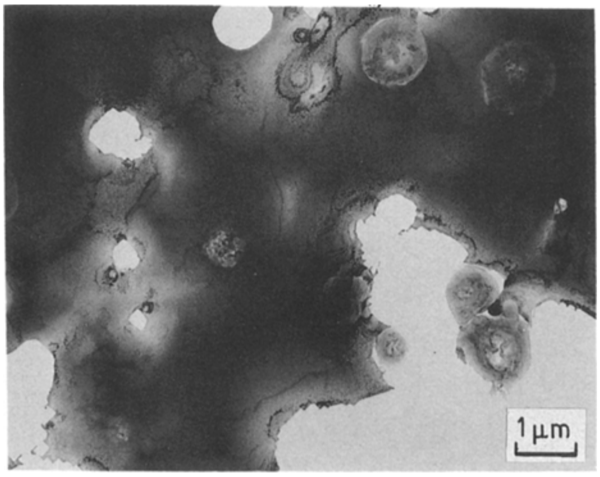

Figure 5 TEM image showing an overview of spherulites in the nickel matrix.

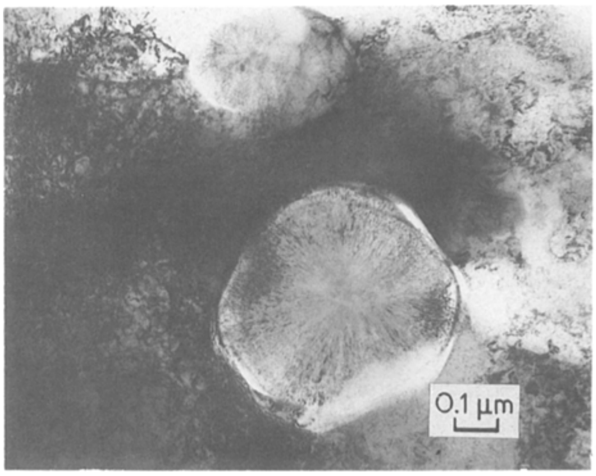

Figure 6 TEM image of smaller spherulite, completely filled with graphite.

Figure 7 TEM image of spherulite showing concentric graphite growth and different core material.

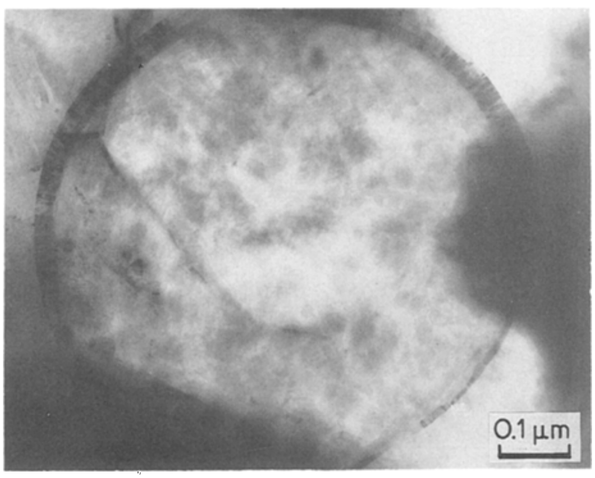

Figure 8 TEM image of graphite rings filled with diamond film.

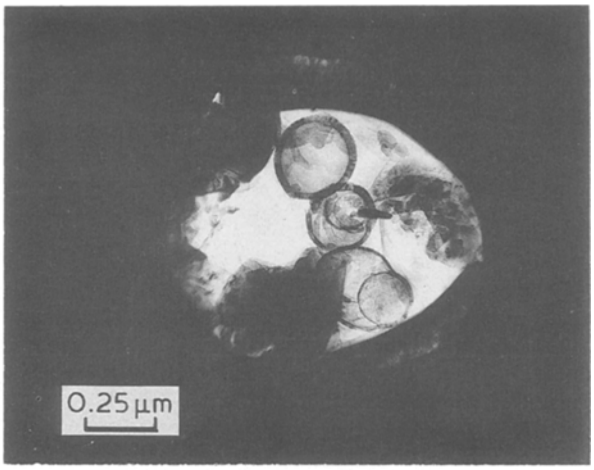

Figure 9 TEM image of a very thin graphite ring with diamond filling.

Under light microscopic observation the spherical particles appeared to be identical to graphite nodules well-known from graphitic cast iron and other graphite-containing melts, including nickel [8]. They displayed the radial growth pattern and the characteristic extinction cross under polarized light. TEM study of the spherulites confirmed that they consisted mainly of graphite, selected-area diffraction of single spherulites giving ring patterns consistent with graphite *d*-spacings.

Figs 5 to 7 show various aspects of how the nodules appear under TEM observation: an overall view at low magnification, a small spherulite completely filled with graphite, and a larger one showing a different morphology at the centre. We observed many other spherulites similar to the latter but with even larger centre portions different from graphite. Many showed no more than a graphite ring surrounding a filmy substance (Figs 8, 9).

Some of the microstructural features observed are similar to those described by Kleiman *et al.* [3], and the spherulite formation may be explained by the kind of processes suggested by the authors for the formation of diamond in a graphite–metal coolant under shock compression. The mechanisms they propose consist, in summary, of a solid–gas–liquid–solid sequence of phase transitions. The key step in this model is the involvement of a transient liquid graphite. However, the existence of liquid carbon is difficult to justify with our composite powder mixtures. If the temperatures were high enough to cause a transformation to a liquid or vapour state of the graphite, the nickel would long be vaporized. In the present work, therefore, we sought a different explanation.

More than a quarter of a century ago, Stadelmaier discussed the growth of graphite spherulites in metallic melts [8]. He proposed that the occurrence of nodular graphite was the result of gas bubbles permeating a metallic melt. In the case of a melt which is supersaturated with carbon, such as graphitic cast iron, graphite crystallizes upon cooling on the

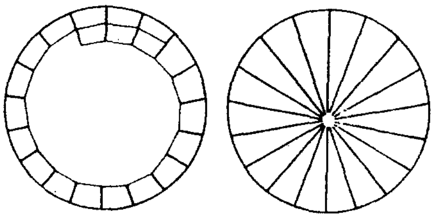

Figure 10 Schematic drawing of facet-like growth of spherulites. From Stadelmaier [8].

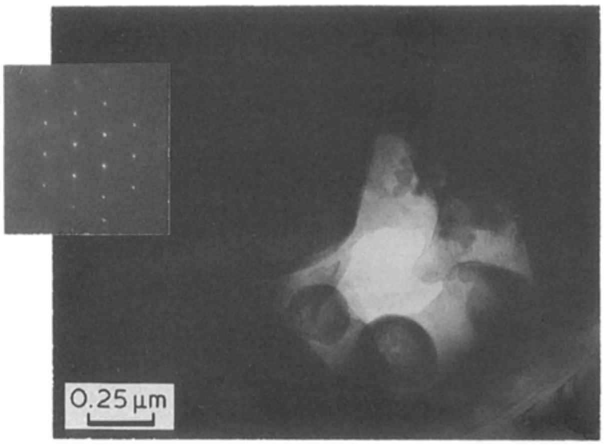

Figure 11 Bright-field image of a spherulite with a diamond core. Inset is the diffraction pattern of the surrounding nickel matrix.

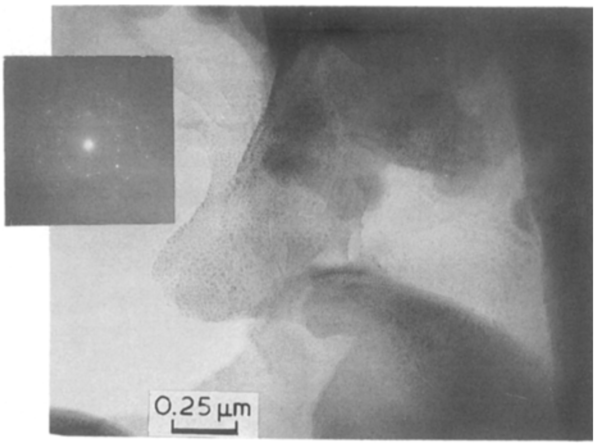

Figure 13 Higher magnification of the same spherulite as in Fig. 11, core area, where the inset diffraction pattern of polycrystalline diamond was taken.

periphery of such bubbles. The periphery is, after all, a metallic surface and a good heat sink. It is known that flake graphite grows along the hexagonal base plane forming elongated crystals, while crystallization of the spherulites is normal to that direction. It occurs facet-like: layer after layer is built until all the carbon is used up or the void is filled. This is schematically illustrated in Fig. 10.

The micrographs shown in Figs 6 and 7 are convincing examples of this model. Additional evidence comes from electron diffraction information: a full spherulite, singled out by the appropriate selected-area aperture, shows a polycrystalline graphite ring pattern, and microdiffraction of part of a graphite spherulite shows arced rings (Fig. 12, inset), a sign of crystallographic orientation. A section of the nodule can be considered as a bundle of nearly parallel crystals which would give rise to such a diffraction pattern.

Similar processes as described in [8] can be expected in the shock-compressed samples if the metallic component melts. Judging from the features seen in Fig. 3, we believe that the temperatures in the reacted area C are high enough to melt the nickel, though not necessarily so high as to melt graphite. The presence of gas bubbles is readily explained considering the large surface area of the original powder particles, as well as the probability of gases trapped in the graphite flakes. CO and CO_2-gases, or even hydrogen-containing gases from the nickel-coating process, could easily result. The large graphite flakes, crumbling and dissolving under shock compression, cause supersaturation of the nickel with carbon.

In our samples diamond was found in two different locations: (1) the centre of spherulites which were not completely filled up with graphite, but which instead showed an electron beam-transparent material (Figs 11 to 14); (2) the flake graphite where hexagonal crystallites appeared (Fig. 15). The orientation of the single crystals within the flake graphite did not allow unequivocal identification by electron diffraction as diamond, because nickel can show the same pattern with almost identical *d*-spacings. However, the polycrystalline ring pattern of the filmy material within the spherulites were determined definitely to be that of diamond by comparing the microdiffraction patterns of nickel, graphite and diamond (Figs 11 to 13 insets) as described below.

1. The distinction of nickel, graphite and diamond is based on the appearance (or lack thereof) of the [2 0 0] reflection. Because diamond has a cubic structure it does not produce the [2 0 0] reflection while nickel with its fcc lattice does. Graphite has hexagonal symmetry, and its first ring is the [0 0 0 2] reflection corresponding to a *d*-spacing of 0.3348 nm.

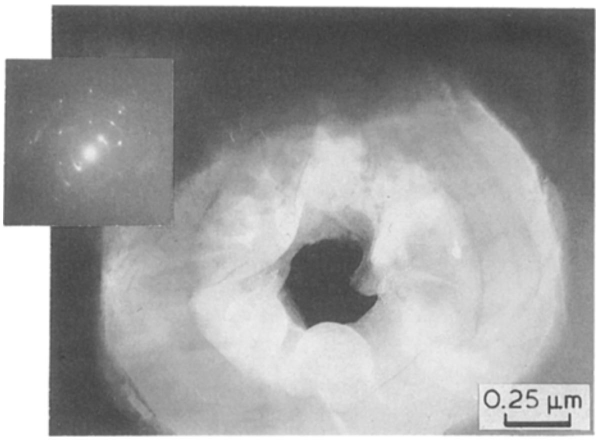

Figure 12 Dark-field image of the same spherulite as in Fig. 11. Inset is the diffraction pattern of the graphite ring portion.

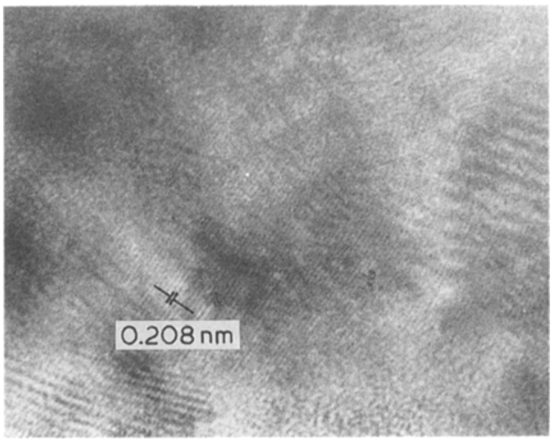

Figure 14 High-resolution TEM image of diamond phase.

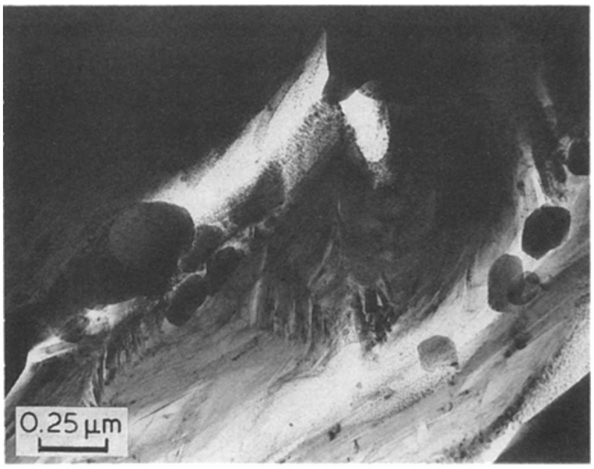

Figure 15 Hexagonal crystallites in flake graphite.

2. Identification of the graphite is made with the help of the camera constant derived from the nickel [1 1 0] pattern (Fig. 11 inset). The first ring of the graphite pattern is the [0 0 0 2] reflection (Fig. 12 inset). A ring corresponding to this reflection or to the [2 0 0] nickel reflection is missing in the diamond pattern shown in the Fig. 13 inset.

3. High-resolution TEM pictures, such as shown in Fig. 14, taken of the diamond film from a spherulite centre, make visible lattice spacings whose widths are consistent with the (1 1 1) diamond lattice plane spacing (Fig. 14).

4. Conclusion

The mechanisms of diamond formation at the centre of spherulites is not yet well understood. The most difficult question is the time of formation in relation to the duration of high-pressure shock loading which lasts only a few microseconds in the present fixture. Within that time span, the carbon dissolves in and diffuses through the nickel to recrystallize out again in two morphologies, graphite and diamond.

The two traditional methods of forming diamond synthetically, one by high pressure, the other as thin films from hydrocarbon gases where the presence of hydrogen is crucial, may play a combined role in the case of our shock-compressed samples. Their unique history, starting as a nickel-coated graphite powder which has undergone an electrolytic process, possibly leaving behind a hydrogen residue, and their subsequent compression under shock loading with all its aspects of pressure waves and temperature rise, leaves room for the interaction of too many factors to invite an easy explanation. If high pressure is the criterion for diamond formation, the mechanism may be the same as that of static processes where nickel serves as a solvent. However, because of the likely existence of CO, CO_2 or even hydrogen gases, we cannot rule out the possibility of diamond formation by other mechanisms well below the graphite–diamond equilibrium line [9].

Observations of spherulites in graphite/metal compacts were reported by other authors [3, 10]. Kleiman *et al.* [3] attribute their existence to the occurrence of a vapour phase caused by electric flash heating superimposed on shock compression. The authors estimate the maximum temperature and pressure as 5000 K and 50 GPa, respectively. Such conditions are substantially higher than the estimates of conditions in our samples. Interestingly, the authors report diamond formation only when flash heating was added during shock compression. The conditions described by Sekine *et al.* [10] were similar in terms of impact velocity, but recovered diamonds were all hexagonal, and no explanation for the spherulites or their significance in diamond formation is attempted.

Although the hexagonal crystals found within the flaky graphite (Fig. 15) in our samples have not yet been identified unequivocally as diamond, we believe that (1) diamond can form in graphite/metal mixtures under shock compression, either through direct transformation or a solvent action of the metal melt, and (2) the threshold conditions need not be of the order of magnitude as those reported earlier.

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