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Diamond formation in aluminium compressed with nickel–graphite under shock loading

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In-situ characterization of powder mixtures of aluminium and nickel–graphite subjected to high-pressure shock-wave compression was performed using optical and transmission electron microscopy. Formation of a polycrystalline diamond phase was observed for the first time as an apparent continuation of graphite fibres. A shear-induced transformation process is suspected. Among various resulting Ni–Al alloy phases NiAl and Ni_3Al were predominant and had the characteristics of rapidly solidified nickel aluminide.

1. Introduction

We have investigated the dynamic compaction of nickel–aluminium and nickel–graphite [1, 2] and have already established the formation of most nickel aluminide phases in the former and a diamond phase in the latter, using a variety of analytical techniques including transmission electron microscopy (TEM). The present work examines the results of recovery shock experiments with powder mixtures of aluminium and nickel–graphite.

The motive for adding aluminium to the nickel–graphite powder which, previously, had been found to form a diamond phase [2] was threefold: one, to gain a higher temperature during the otherwise identical shock conditions by inducing the exothermic reaction between nickel and aluminium; two, to see whether the precipitation of carbon in the metal is influenced by the strong affinity of aluminium to carbon in a nickel matrix; three, to gain insight into the timing of the diamond formation as it relates to the time-scales of nickel aluminide formation.

2. Experimental procedure

Experimental conditions have been described elsewhere [2]. Mixtures of aluminium and nickel-coated graphite powders were pressed to a theoretical density of 50 to 60% in a stainless steel capsule. The amount of aluminium was chosen to correspond to the stoichiometric ratio of Ni_3Al. Then, an iron flyer plate accelerated by a mousetrap-type explosive plane-wave generator was impinged on the capsule at velocities of 1.1 and 1.6 $\mathrm{km\,s^{-1}}$ (Fig. 1).

The exact loading conditions of pressure and temperature are not known, but it was previously observed [2] that a sample compacted at 1.1 $\mathrm{km\,s^{-1}}$ without aluminium showed no sign of bulk melting of the nickel powder. At 1.6 $\mathrm{km\,s^{-1}}$, nickel in the bottom half of the sample appeared to have melted. Since the nickel aluminide reactions took place under shock loading, the heat of reaction is high enough to melt NiAl even at the impact velocity of 1.1 $\mathrm{km\,s^{-1}}$.

In the previous paper a diamond phase was found only in the sample that was shock-loaded at 1.6 $\mathrm{km\,s^{-1}}$, indicating that the solution of carbon in nickel was an important step in the formation of diamond. But in the present investigation, with the addition of aluminium, a diamond phase was found in both specimens, impacted at 1.1 and 1.6 $\mathrm{km\,s^{-1}}$ respectively, provided that the initial tapping compression was to 50% of theoretical density.

3. Results

Metallographic study preceded TEM examination of the samples. By this low-magnification method none of the graphite spherulites which had been the site of the diamond phase in the nickel–graphite sample were found. Alloying between the two metals was observed: mostly NiAl and Ni_3Al in the sample compacted at 1.6 $\mathrm{km\,s^{-1}}$, and various Al-rich phases beside NiAl and Ni_3Al in the sample compacted at 1.1 $\mathrm{km\,s^{-1}}$. Alloying reactions appeared to have been completed in the first sample. The observation of various stages of the reactions in the second may be attributed to a lower shock-induced temperature.

TEM investigation of the two samples did confirm the presence of spherulites, though they were less frequent, much smaller and had apparently none of the graphite-ring-with-diamond-centre characteristics seen earlier (Figs 2 and 3). Mostly, they appeared in the form of clusters of embryonic spherulites which

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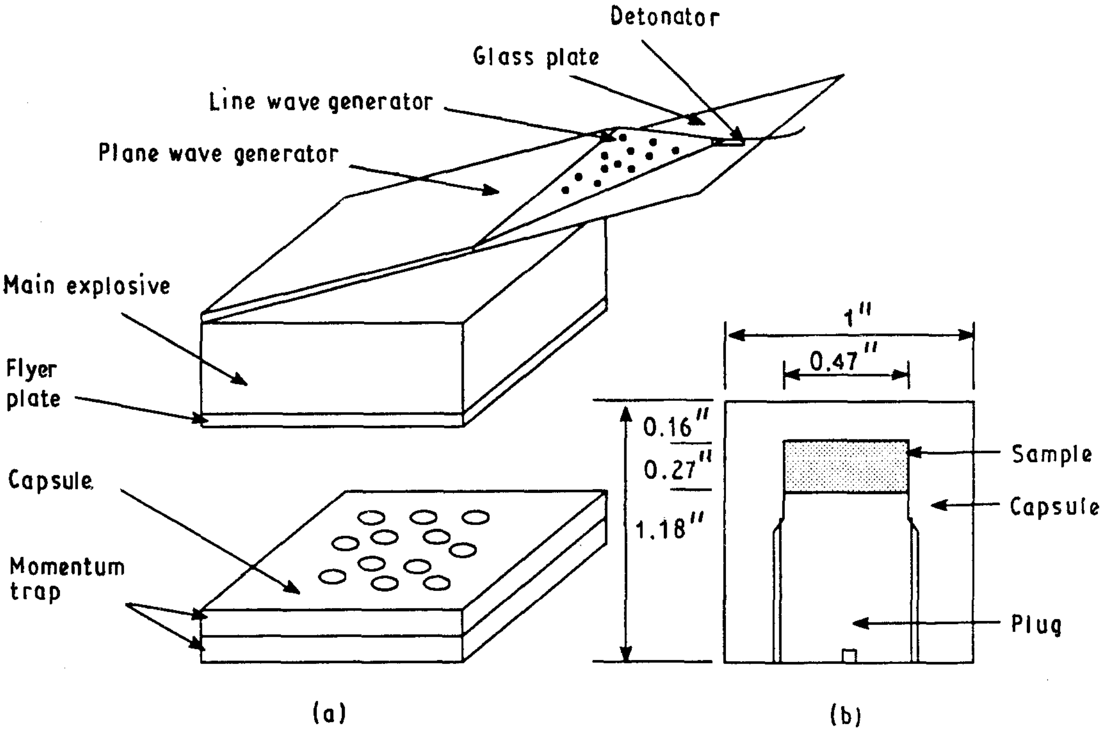

Figure 1 Sketch of mousetrap-type plane wave generator used in shock loading: (a) plane-wave generator and momentum trap recovery system, (b) stainless steel capsule. 1″ = 25.4 mm.

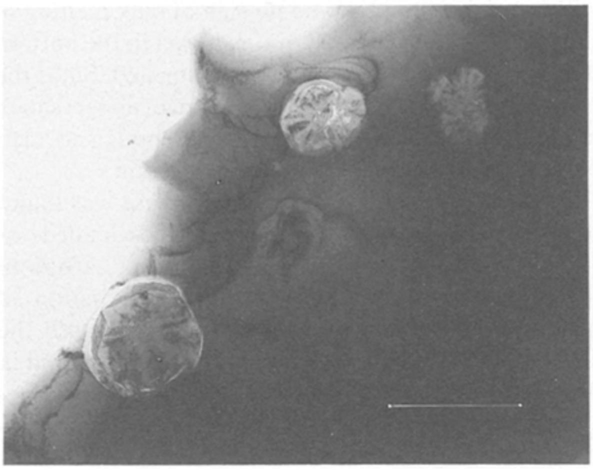

Figure 2 Graphite spherulites. Bar = 1 μm.

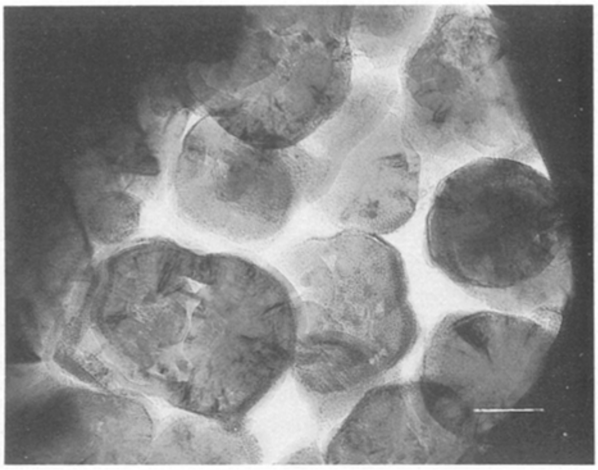

Figure 4 Nest of embryonic spherulites. Bar = 1 μm.

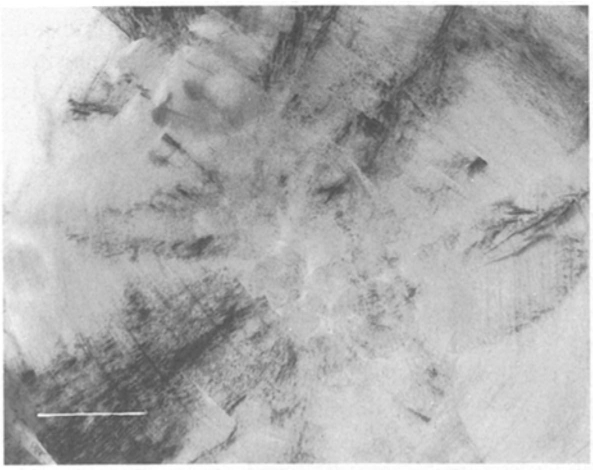

Figure 3 Graphite spherulite showing mini-spheres at centre. Bar = 100 nm.

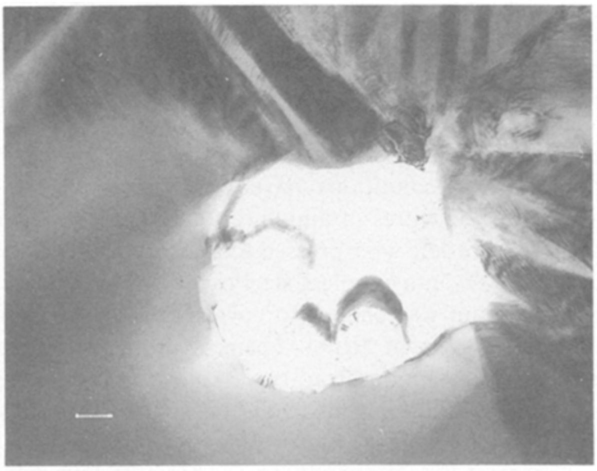

Figure 5 Nest of embryonic spherulites located between nickel phase and NiAl-martensite. Bar = 1 μm.

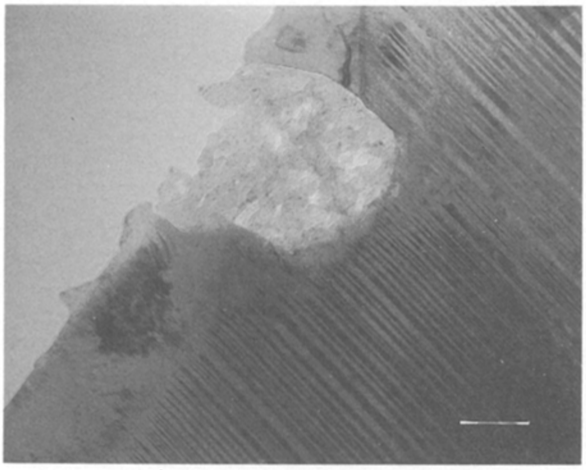

Figure 6 Nest of embryonic spherulites or diamond crystallites. Bar = 100 nm.

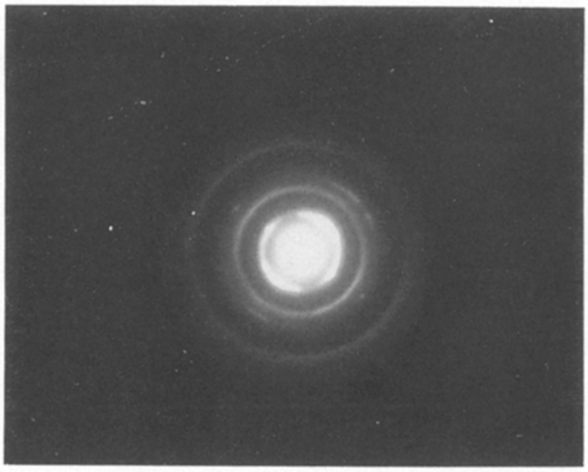

Figure 8 Diffraction pattern of perturbed graphite, showing nearly random orientation.

were nestled at the metal phase boundaries, mainly between nickel and nickel aluminide (Figs 4–6). It is our speculation that the lower frequency of spherulites and their small size may be due to the preferred binding of carbon by aluminium rather than its solution in the nickel matrix. Evidence of a diamond phase was not found in connection with the spherulites. If it exists there (the spherulite in Fig. 3 and the cluster in Fig. 6 are good candidates for containing the diamond phase), the areas were too small for us to identify it.

Both specimens displayed a phenomenon new to us: a change in the appearance of the graphite flakes. The normally parallel fibres of the flakes were disturbed in many places as if they had experienced violent turbulence (Fig. 7). A diffraction pattern of such an area shows mostly the full rings of random orientation and only a hint of the arcs of preferred orientation (Fig. 8) which is typical for the normal graphite flakes. The appearance of turbulence-caused shearing of the graphite flakes in the present experiment may be explained by the large relative velocity that can occur between aluminium and nickel–graphite composite powder.

Close scrutiny of these disturbed regions led to the discovery that the individual graphite fibres seem to "dissolve" into another morphology at the edge of the disturbed flakes (Figs 9 and 10). This new phase did not match any of the metallic compounds. Electron diffraction proved it to be polycrystalline diamond. Both nickel and Ni_3Al are face-centred cubic (f.c.c.),

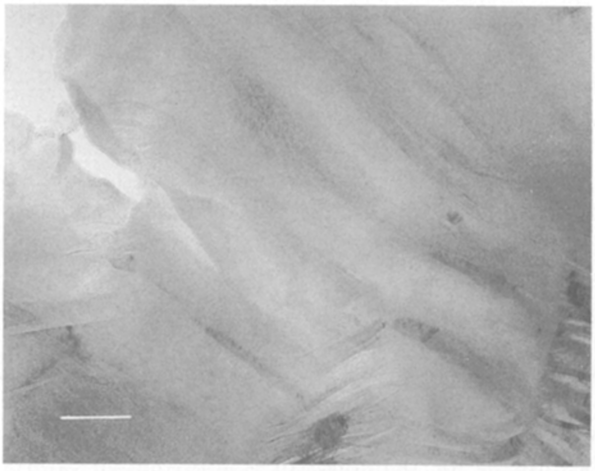

Figure 9 Transition from graphite fibres to diamond phase. Bar = 100 nm.

Figure 7 Perturbed graphite flake. Bar = 100 nm.

Figure 10 Transition from graphite fibres to diamond phase. Bar = 100 nm.

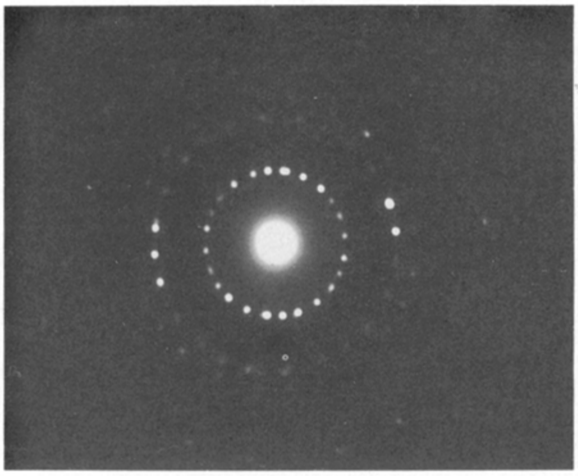

Figure 11 Diffraction pattern of twinned diamond crystal.

and though both have (1 1 1) reflections with very similar *d* spacings to those of diamond, the missing (2 0 0) reflection of the cubic diamond is an easy distinguishing mark. The strong (1 1 1) reflection of the randomly oriented graphite has a significantly larger *d* spacing (0.335 nm) and thereby it cannot be mistaken for diamond, nor can aluminium or any of the other nickel aluminides.

This diamond phase was found extensively in both samples, impacted at 1.1 and 1.6 km s^{-1}. The diffraction pattern showed that the crystallites were often large enough to cause spotty rings. One pattern has a high symmetry of these spots, suggesting a twinned crystal (Fig. 11). The corresponding bright-field image (Fig. 12), however, is not very different from other diamond-phase areas (Figs 13 and 14). One diffraction pattern is curiously oval (Figs 15 and 16), and it is presumed that a larger nearby nickel region might have caused a distortion of the electron beam due to the magnetic properties of nickel.

Just as the spherulite clusters could be found between nickel and NiAl-martensite phases, this was the location of the diamond areas too, though always adjoining graphite. Fig. 15 shows the diamond phase growing from a graphite flake on the right. A lower magnification of the same region (Fig. 16) offers a view of the larger context with nickel at the top of the image, martensite at the upper left, diamond in the middle and graphite at the right.

Additional findings through TEM analysis include the alloying of nickel and aluminium, mostly in the

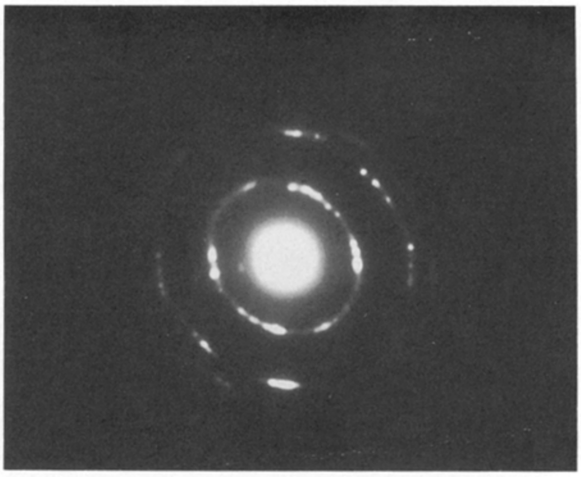

Figure 13 Diamond diffraction pattern (beam distortion presumed to be due to magnetic nickel phase nearby).

Figure 14 Bright-field image to Fig. 13. Bar = 100 nm.

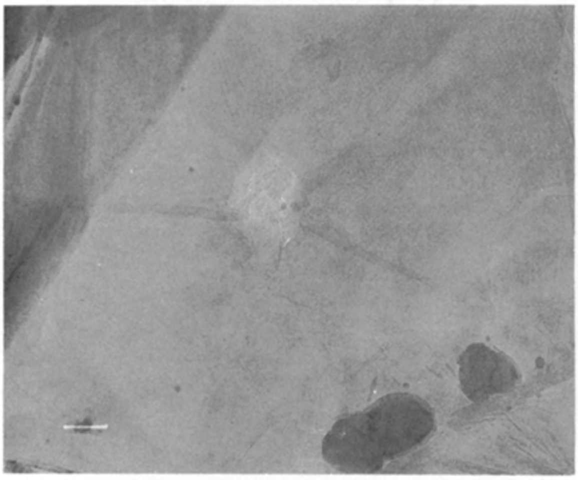

Figure 12 Bright-field image to Fig. 11. Bar = 100 nm.

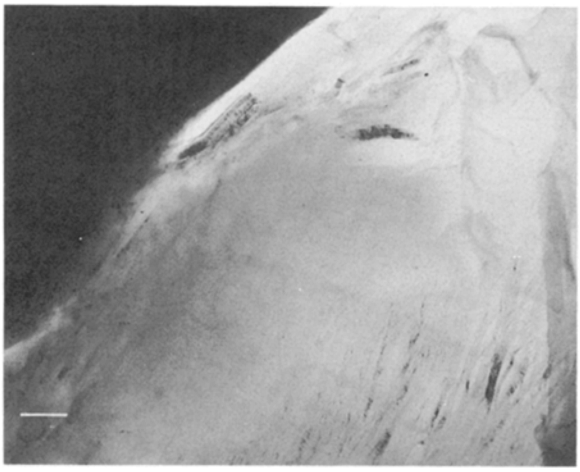

Figure 15 Diamond phase with surrounding microstructure. Bar = 100 nm.

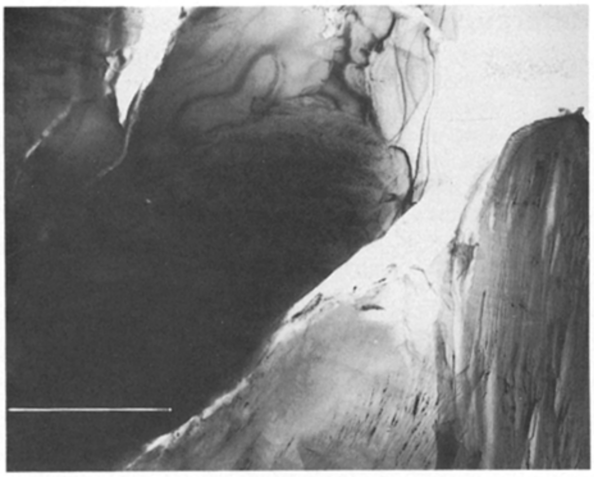

Figure 16 Lower magnification of Fig. 15 showing larger context of surroundings. Bar = 0.1 μm.

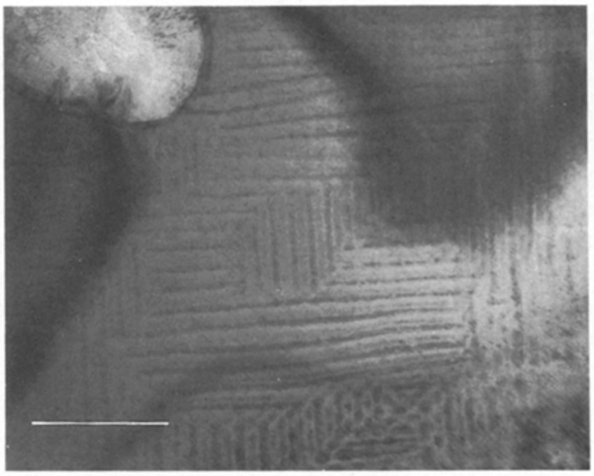

Figure 19 Tweed structure of NiAl phase. A spherulite is visible in the upper left corner. Bar = 100 nm.

form of NiAl-martensite which is well known as a structure resulting from shear stresses due to rapid cooling. In the shock-loaded samples this phase grows dendritically into a nickel matrix (Fig. 17) and has the typical herring-bone appearance of the martensite plates featuring micro-twinning (Fig. 18), and sometimes that of the so-called tweed structure (Fig. 19). These morphologies of nickel aluminide are known and have been extensively studied in rapidly solidified nickel aluminides [3, 4].

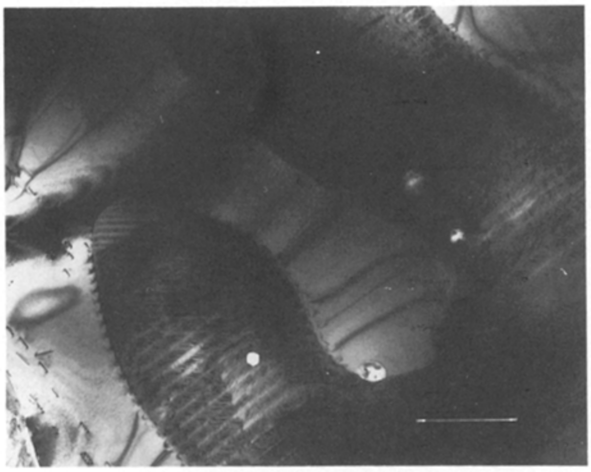

Figure 17 Dendritic growth of NiAl-martensite in nickel matrix. Bar = 1 μm.

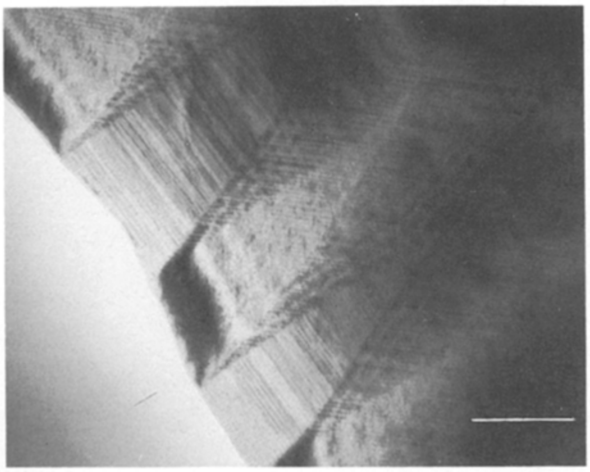

Figure 18 Higher magnification of martensite. Bar = 100 nm.

The phenomenon of the perturbed graphite reminded the authors of an earlier observation in the nickel–aluminium study. In that investigation isolated "swirls" of the high-melting NiAl were found. Since NiAl has a wide compositional range, its coloration under optical microscopy varies greatly with the relative aluminium content. These colour shadings could be seen stirred together in small whirlpools. Such turbulences attest to the high mechanical stresses the material undergoes during explosive compaction. The temperatures reached with this process easily exceed the melting point of NiAl (1638 °C).

It is our current speculation that a diamond phase in the highly disturbed region is caused by a direct lattice transformation under the action of high shear forces during shock loading. This may be possible by a mechanism such as the one described by Kleiman *et al.* [5] where one carbon atom in the graphite molecule switches position to form the diamond molecule (so-called "puckering"). However, we cannot certainly rule out the possibility of an amorphous transition between the graphite fibres and the diamond phase. High-resolution TEM may resolve this question.

4. Conclusion

The results of this experiment indicate that there exists more than one mechanism of diamond formation under shock loading and that the threshold impact velocity is far smaller than the often quoted value of about 2.5 km s^{-1}. In the case of nickel–graphite composite powders, evidence shows that carbon diffused through the molten nickel, precipitated on the periphery of gas bubbles as graphite and formed spherulites which in many cases contained a diamond centre. There is speculation that the presence of trapped hydrocarbon gases in the graphite might have had an influence on the diamond formation. In the present case, there is evidence of a non-diffusive mechanism through a direct lattice transformation or amorphization and recrystallization.

Although the exact calculation of loading conditions is difficult for a variety of reasons, an estimate of the maximum pressure attained in the sample impacted at 1.1 $\mathrm{km\,s^{-1}}$ is about 10 GPa. The maximum temperature probably rose to less than 2000 °C, and reaction speeds compare to those in splat-cooled nickel aluminides.

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