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Formation of bridges between diamond particles during sintering in molten cobalt matrix*

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Large diamond particles of about 700 μm size mixed with 70 wt % fine cobalt powder have been sintered at 5.25 GPa and 1500 °C after wrapping in zirconium foil. During the sintering treatment faceted inter-particle bridges form, and their pale yellow colour in contrast to the dark yellow colour of the original diamond particles indicates that the bridge is a new phase reduced in nitrogen content because of the gettering effect of the zirconium foil. The morphological characteristics of the bridge and the adjacent particles indicate that the bridge is formed by migration of the inter-particle grain boundary and solution–reprecipitation through the liquid cobalt matrix. It is possible that these processes are induced by the coherency strain energy produced by nitrogen diffusion from the region ahead of the retreating boundaries, as has been observed in metal systems.

1. Introduction

Compacts of diamond powder mixed with iron-group metal powders are usually sintered at about 6 GPa and 1550 °C to be used as cutting tools or rock drilling bits. Cobalt powder at volume fractions below 5% is used most often. For the sintering treatment the compacts are usually wrapped in zirconium foil in order to separate the compacts from the pressure medium, which is usually molten NaCl. Because of the strong tendency to form zirconium nitride, zirconium is known to have a strong gettering effect on nitrogen, which is usually present in diamond at small concentrations [1]. It is thus possible that the reduction of nitrogen in diamond produces a relatively strong chemical driving force for morphological changes during the sintering treatment.

The purpose of this work is to investigate the formation of bonds between the diamond particles during the sintering. In spite of its importance in determining the properties, its mechanism is not still well understood, and, in particular, the possible effect of nitrogen gettering by zirconium on the bond formation has not been clarified. In order to facilitate the observation, a model system of coarse diamond particles (about 700 μm) mixed with a large amount of cobalt (70 wt % or about 50 vol %) was selected.

2. Experimental procedure

Diamond particles of nearly cubo-octahedral shape and about 700 μm size were obtained from De Beers Co. These were dry-mixed by stirring by hand with high-purity cobalt powder of about 1 μm size at 3 to 7 ratio by weight. As illustrated in Fig. 1, the powder mixture was separated from the molten NaCl pressure medium by wrapping in a zirconium foil, and sintered in a belt-type high pressure apparatus at 1500 °C and 5.25 GPa. The sintered specimens were leached in concentrated hydrochloric and sulphuric acids in order to remove, respectively, the cobalt matrix between the diamond particles and the graphite at the diamond surface.

3. Results and discussion

After relatively short sintering treatments the diamond particles became weakly bonded to each other. After 1 h of sintering treatment, the specimen disintegrated after the acid treatment to remove the matrix. When sintered for longer periods, distinct bridges were observed to form between the particles as shown in Fig. 2 at low magnification and in Figs 3 and 5 at high magnifications. In Fig. 2 two distinct intergranular bridges are marked A and B. The scanning

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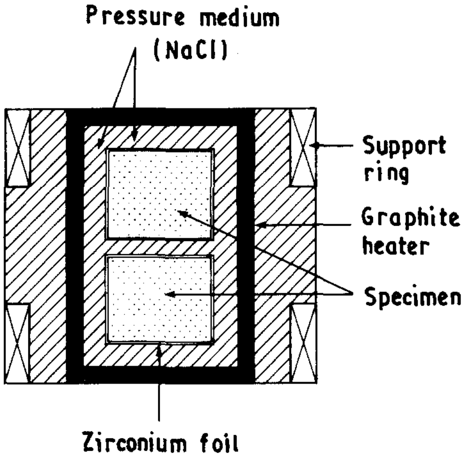

Figure 1 Schematic experimental set-up for sintering.

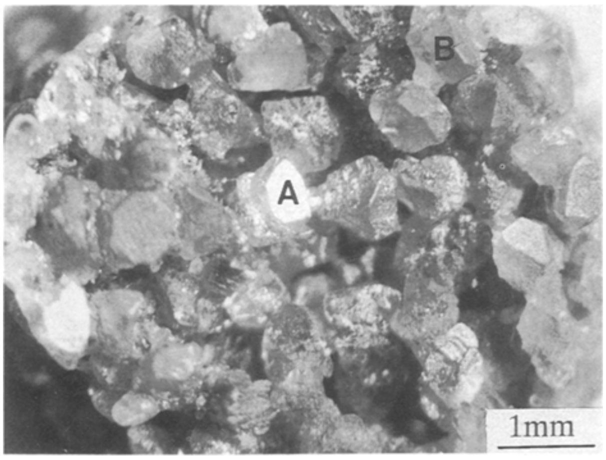

Figure 2 Diamond–70 wt % Co sintered at 5.25 GPa and 1500 °C for 12 h.

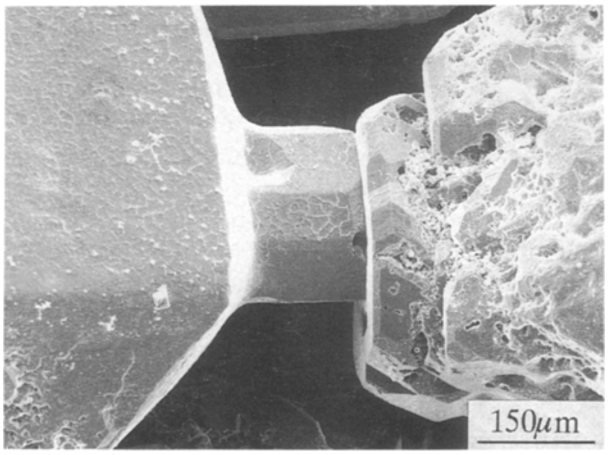

Figure 3 The inter-particle bridge A in Fig. 2 at a higher magnification.

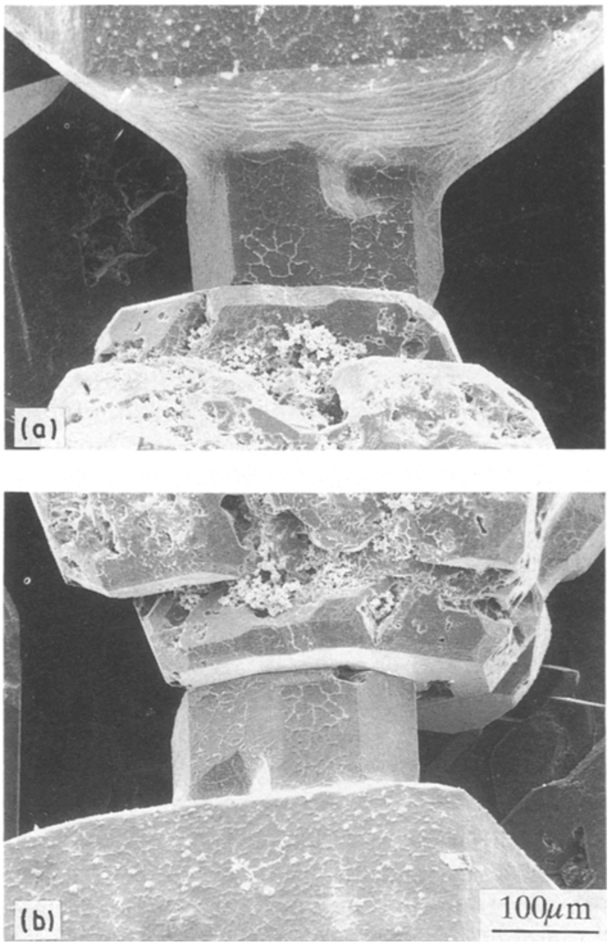

Figure 4 (a) Left-hand side and (b) right-hand side of bridge A in Fig. 3 viewed at different angles.

electron micrographs of bridge A are shown in Fig. 3 at a higher magnification. It appeared that at one end of the bridge A (left-hand side in Fig. 3 and top side in Fig. 4a) there was no boundary between the original particle and the bridge, while at the other end (right-hand side in Fig. 3 and top side in Fig. 4b) there was clearly a boundary. Since this boundary region was not attacked during the acid treatment, it appeared that these boundaries were grain boundaries.

At certain angles of observation a colour contrast between the bridges and the original particles was observed as indicated by an arrow in Fig. 5 for bridge B in Fig. 2 at a higher magnification. Since nitrogen produces a yellow colour in diamond [2], the bridge region which had a pale yellow colour (indicated the arrow in Fig. 5) appears to be lower in nitrogen than the original grains. Throughout the specimen there was a tendency for the bridges to grow from the particles near the specimen surface to those in the inner region. This preferential growth direction may be related to the expected rapid reduction of the nitrogen activity at the specimen surface adjacent to the zirconium foil at the initial stage of the sintering treatment.

These observations strongly indicate that the bridges are formed by migration of the grain boundaries and by dissolution of the retreating particle and re-precipitation at the bridge through the liquid matrix. This mechanism of bridge formation appears to be furthermore consistent with the surface characteristics shown in Figs 3 and 4. The surfaces of the bridge and the particle on which it is growing are relatively smooth and distinctly faceted. In contrast, the surface of the retreating particle is very rough with pits and channels, which are known to be the characteristics of dissolving diamond surfaces [3]. This contrast in the

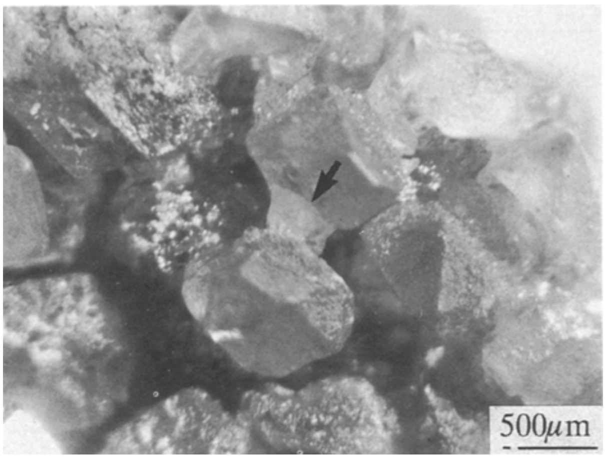

Figure 5 The inter-particle bridge B in Fig. 2 at a higher magnification.

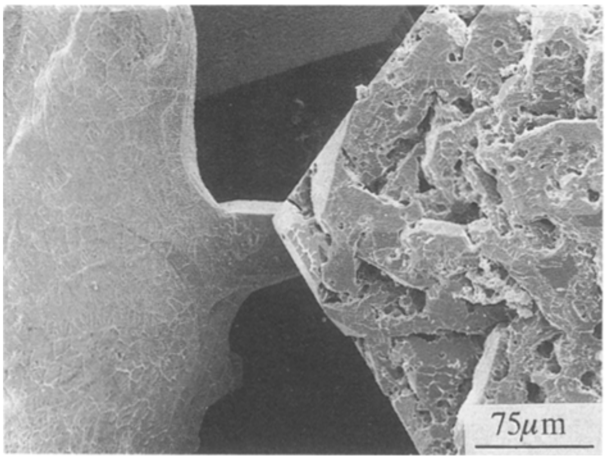

Figure 6 Another inter-particle bridge in the specimen shown in Fig. 2.

surface morphology was quite general, as can be seen in another bridge shown in Fig. 6.

The observed bridge formation thus shows similarities to the chemically induced grain-boundary migration and solution–reprecipitation through a liquid matrix which have been recently observed in a number of metal systems (e.g. [4–10]). Since zirconium is expected to reduce the nitrogen content in the diamond, there will be a chemical driving force to form a new diamond phase with nitrogen concentration lower than that in the original particles. This chemical driving force can apparently cause the growth of a new equilibrium solid at the expense of the original one by interface migration rather than a lattice diffusion process.

In this type of migration, which has been referred to as either chemically or diffusion-induced boundary migration, it has been proposed that the solute atoms can diffuse ahead of the migrating boundaries, dissipating much of the chemical driving force for equilibration and producing a diffusion zone which is coherent with the lattice of the retreating grain (e.g. [11–14]). This coherency strain was demonstrated to be the driving force for boundary migration in a series of critical experiments on Mo–Ni alloys (e.g. [15–18]). The loss or gain of nitrogen at the interface of a diamond can produce a coherency strain, since the lattice parameter is known to change significantly with nitrogen concentration [1]. It is not possible, however, to estimate the coherency strain in these experiments, since the nitrogen concentrations in the initial grains and in the newly formed bridge could not be measured.

4. Conclusions

The formation of bridges between diamond particles during sintering in the presence of zirconium appears to be caused by the gettering of nitrogen by zirconium, and hence shows similarities to the chemically induced boundary migration which has been observed in metal systems. Although the diffusional coherency strain energy arising from the lattice parameter change with nitrogen content can drive the migration, the nature of the driving force could not be ascertained from these observations. It is possible that such a bridge formation can significantly affect the properties of sintered diamond pieces.

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