JOURNAL OF MATERIALS SCIENCE 24 (1989) 942-950

Thermal degradation of sintered diamond compacts

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A method was devised to subject sintered diamond compact drill blanks to rapid thermal excursions, and the properties of the compact were studied after heating. It was found that thermal degradation as detected by rock-cutting tests and polished metallographic cross-sections could be correlated with acoustic emissions of the compact during heating. The drill blanks exhibited a delayed failure phenomenon which followed an Arrhenius relation with an activation energy of 327 kJ mol^{-1}, and this behaviour was attributed to the initiation of graphitization of the sintered diamond compact.

1. Introduction

The purpose of this investigation was to study the time–temperature relations involved in the thermal degradation of polycrystalline sintered diamond compact drill blanks, whose nature has been previously described [1, 2]. Such heating excursions can be encountered, for example, when bonding the drill blanks to carbide studs and the subsequent attachment of these drill blanks to bit bodies. Thermal degradation may also be encountered in service, but these heating conditions are largely unknown and are superimposed on severe wear conditions; hence, they are not amenable to controlled laboratory experiments. The work to be described involved the rapid heating of drill blanks by the use of infrared heat and the monitoring of this heating cycle by acoustic emission. The degree of thermal damage was assessed by rock-cutting tests; in addition, metallographic cross-sections of the diamond/carbide interface were examined to attempt to determine the nature and location of thermally induced damage. These studies were aimed at gaining a more fundamental understanding of thermally induced damage in diamond compacts.

The majority of the experiments was performed on diamond compacts with a relatively coarse grain size, of the order of 170 μm. A limited number of finer grained (grain size $\sim 1.5\,\mu$m) compacts were examined, primarily to compare their fracture characteristics and time–temperature relations to the coarse-grained material. Finally, several heating tests were performed on the coarser grained compacts with the carbide substrate removed, either by machining or acid leaching. These experiments were conducted in order to clarify the degradation mechanisms involved.

2. Experimental procedure

The method chosen to heat the diamond compacts was infrared heating in an inert atmosphere. This technique allowed heat to be supplied directly to the diamond table and resulted in a relatively rapid thermal excursion. The temperature was measured by two 180° opposed thermocouples attached to the carbide directly below the diamond table. In general, the temperature difference did not exceed 5° C. The compact was placed on the bottom of a quartz tube, and an atmosphere of flowing nitrogen was used. In a typical heating test to, say, 800° C, temperature was reached in about 40 sec, and held within $\pm 10°$ C for the required time. The apparatus is shown in Fig. 1.

Acoustic emissions were detected by means of a Dunegan (San Juan Capistrano, California) D140B transducer attached to a 1.6 mm diameter waveguide which in turn was in contact with the diamond table. The acoustic emission analyser used was a Physical Acoustics (Princeton, New Jersey) Model 3004 Analyser operating at an overall gain of 72 dB (40 dB at preamplifier, 32 at amplifier). The preamplifier had a 40 kHZ high pass and 100 kHZ low pass filter, while the amplifier had a 50 to 200 kHZ band pass filter. The acoustic emission response parameter used to characterize the diamond compacts was cummulative total events.

The procedure for conducting wear tests on diamond compacts has been fully described previously [3]. The test conditions for the present wear tests were: speed 2.29 m sec^{-1} (450 ft min^{-1}); depth of cut, 0.51 mm (0.020 in.); distance/revolution of feed, 0.31 mm (0.012 in.); negative back rake angle, 20°; side rake angle, 0°; coolant, water base at 25.41 litre min^{-1} (6.7 gal min^{-1}); work piece, nugget sandstone.

The wear rate was computed as described previously [3] as the volume of diamond removed per metre of cut. The only difference between these tests and those previously described is that in the present case the wear was measured for three units (of the order of 4500 m) of sliding distance per wear flat in order to obtain an average value well into the diamond and avoid errors introduced by edge imperfections. For

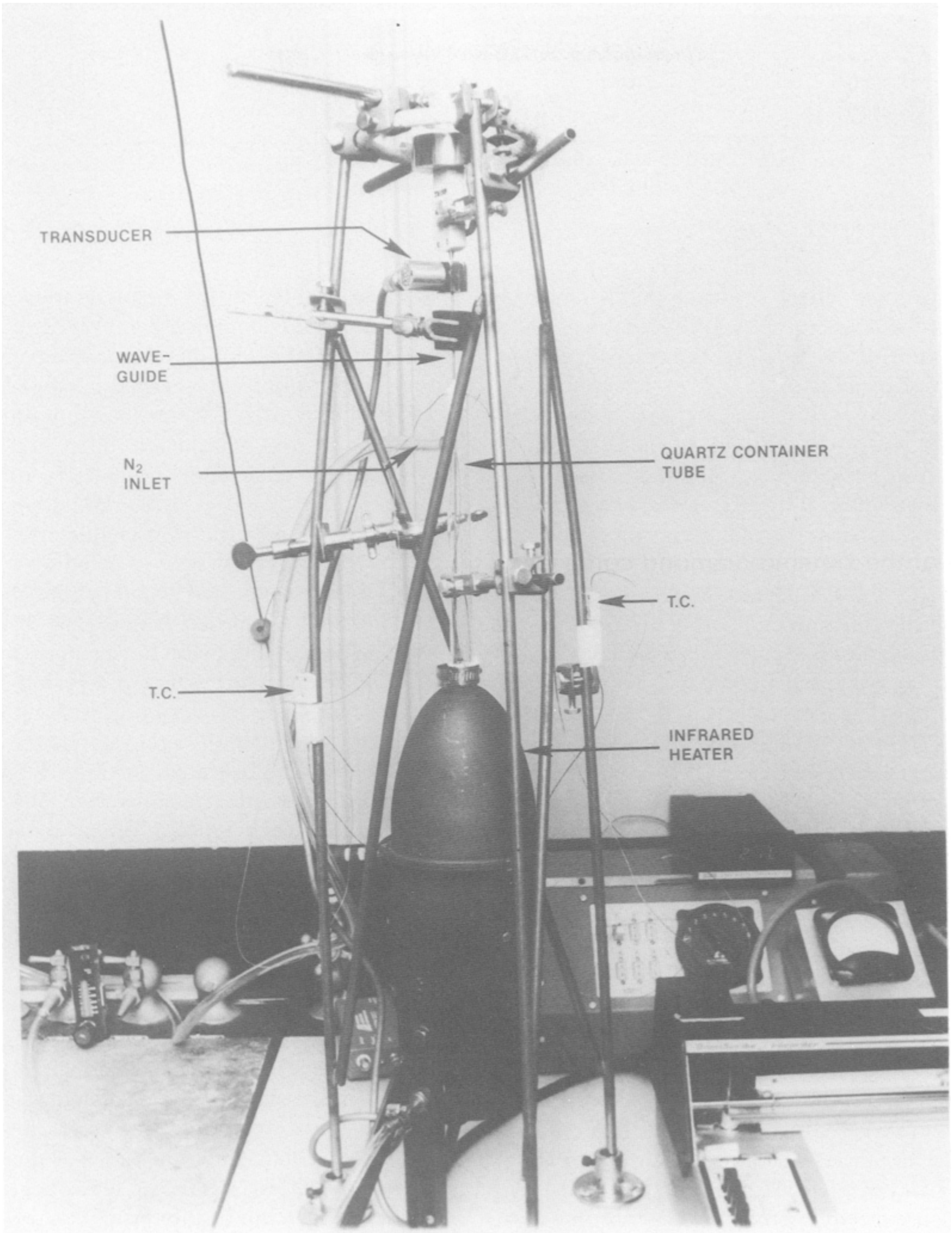

Figure 1 Infrared heating arrangement. T.C. = thermocouple.

the case of badly thermally damaged compacts, only one unit of sliding distance was necessary.

3. Experimental results

3.1. Wear and acoustic emission

Figs 2 and 3 show typical AE data for diamond compacts that were and were not degraded as a result of heating. For the case of a compact which did not degrade as a result of heating to about 830° C and immediately cooled, acoustic events were first detected at ~400° C, increased and then levelled out as the temperature was raised to 830° C, at which point the power to the infrared source was turned off. This behaviour is illustrated in Fig. 2. The cause of these low-temperature (~400 to 830° C) acoustic events is not known, but based on subsequent wear tests they

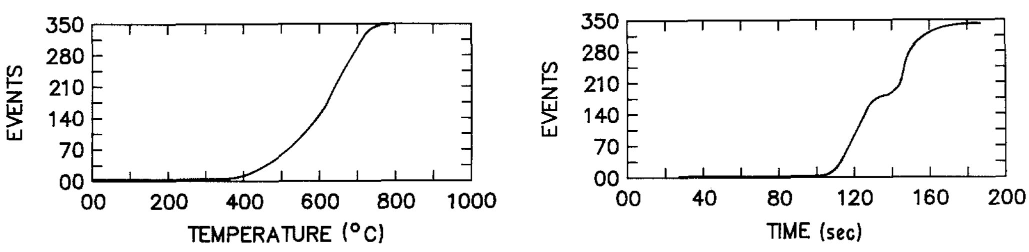

Figure 2 Event–temperature and event–time history of a coarse-grained drill blank heated to 830° C and not thermally degraded.

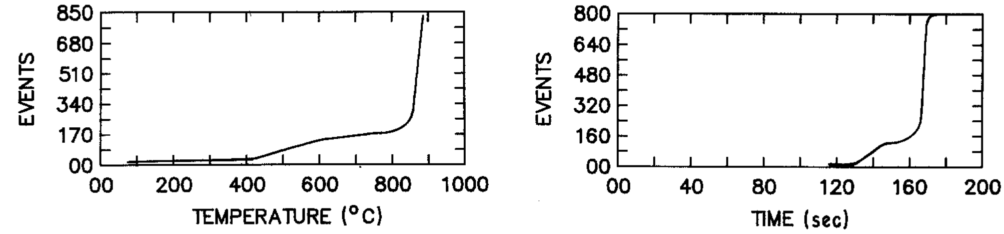

Figure 3 Event–temperature and event–time history of a coarse-grained drill blank heated to 910° C and thermally degraded.

did not adversely affect compact performance. By contrast, if the temperature was raised above 830° C, at some temperature ~900° C the acoustic emission rate increased by a factor of ~70 (~0.4 events/° C to ~30.0 events/° C). This is an indication of thermal damage and is illustrated in Fig. 3. The effect of holding at a given temperature will be discussed in the following section but it may be noted that a compact can survive a transient thermal excursion to ~870° C, but holding for 30 to 60 sec at such a temperature in general led to thermal degradation.

The acoustic emission and failure behaviour for the fine-grained diamond compacts was quite different. Unlike the coarse-grained compacts, these compacts exhibited little, if any, acoustic activity prior to 800° C, and then showed a rapid and then catastrophic increase in the emission rate. This is illustrated in Fig. 4. This higher level of acoustic response is due to the formation of radial and circumferential cracks which will be discussed subsequently. Only one wear test was conducted on a fine-grained compact, and no effect of heating on wear rate was observed. These fine-grained compacts either failed catastrophically or were essentially undamaged.

Considering only the coarse-grained diamond drill blanks, a plot of the acoustic events obtained for each test is plotted against wear rate in Fig. 5. This plot includes all data independent of temperature or time. As anticipated, three distinct regions were found. Up to about 400 acoustic events per test, low wear (of the order of $5.4 \times 10^{-11}\,cm^3\,cm^{-1}$) was observed, irrespective of test temperature. Above about 1000 events, a region of high wear (greater than about $5.4 \times 10^{-9}\,cm^3\,cm^{-1}$), was obtained with more scatter present in the data. Between 500 and 1000 acoustic events, a transition region between high and low wear was observed. As expected, low and high wear rates were generally associated with low and high test temperatures and/or times.

3.2. Delayed failure phenomenon

As indicated above, holding at temperatures above ~860° C for relatively short times led to compact thermal degradation. However, longer heating times are also of interest. Bit manufacturers may torch or furnace braze diamond compact drill blanks into their bits, and definition of time–temperature profiles that do not introduce thermal damage is of interest. More importantly, a wider spectrum of experimental hold times was considered necessary to establish more general time–temperature degradation relations. Consequently, a series of compacts were heated for longer times and their wear characteristics examined.

The results of these tests revealed what we believe is a previously unreported phenomenon. Diamond compacts exhibit a delayed failure time with respect to thermal degradation, with the incubation period varying with temperature. There is a period during which a diamond compact can be heated without damage occurring, and then thermal degradation commences. This effect is illustrated in Fig. 6. As discussed previously, acoustic emissions were detected at about 400° C, and then levelled off at temperatures less than about 850° C. For about 400 sec, this compact behaved normally. However, at 400 sec acoustic activity, as shown in Fig. 6, increased sharply between 400 and about 800 sec, and then gradually diminished for the duration of the test. The total accumulated events were 1690 and the compact was severely degraded as detected by a wear test.

Subsequent tests indicated that this incubation period for the onset of thermal damage was shorter for higher temperatures and longer for lower temperatures. At 750° C, for example, the time was greater than the 1 h test duration. This suggested that an Arrhenius relation of the form

$$t = K\,e^{Q/RT}$$

could apply to these data, where t is the time, K a constant, Q an activation energy for the process, R the gas constant ($8.31\,J\,K^{-1}\,mol^{-1}$), and T the absolute temperature. Fig. 7 shows a plot of the applicable data, and within the accuracy of the data a straight line is obtained when $\ln t$ is plotted against $1/T$. The correlation coefficient was calculated to be 0.84. Experimental errors include the accurate determination of the onset of increased acoustic activity,

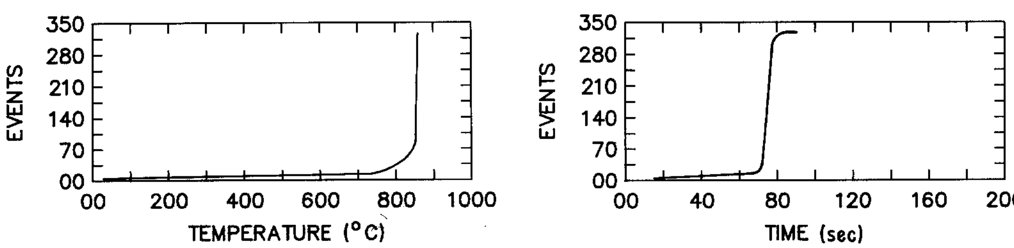

Figure 4 Event–temperature and event–time history of a fine-grained drill blank heated to 890° C and thermally degraded.

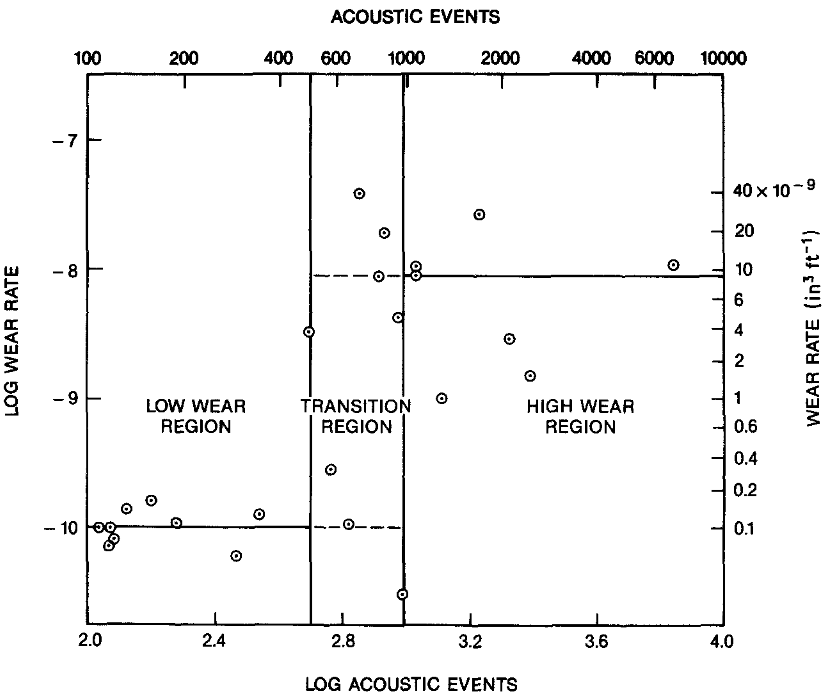

Figure 5 Acoustic events plotted against wear rate.

maintaining the proper temperature, and the variability between individual diamond compacts.

The physical significance of the calculated activation energy, $327\,\mathrm{kJ\,mol^{-1}}$, is not fully understood. It is lower than the activation energy for the graphitization of diamond, which has been reported to be $730 \pm 50\,\mathrm{kJ\,mol^{-1}}$ [4]. However, diamond compacts differ chemically from natural diamond, and it does seem clear that the compact degradation is initiated by some type of a chemically activated process which subsequently leads to diamond breakage. This will be discussed in more detail in Section 4.

Considering the fine-grained diamond compacts, only a few tests were conducted at longer times in order to determine if these compacts also exhibited delayed failure behaviour, and as shown in Fig. 8, they did. The difference in fracture behaviour of compacts heated for long and short times was striking. In both cases, radial and circumferential cracking was observed; for the case of short heating times these cracks formed suddenly and were few in number as shown in Fig. 9. In contrast, for longer heating times the crack took a much longer time to develop (~ 10 sec compared to ~ 500 sec). The cracking pattern was also different, as shown in Fig. 10. The presence of a far larger number of cracks should be noted corresponding to the longer time for them to develop. This suggests the presence of a larger number of nucleation sites and is consistent with a chemically activated process.

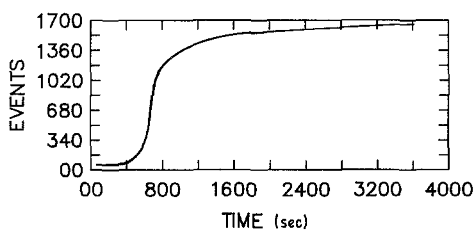

Figure 6 Event–time history of a diamond compact heated at 800° C and exhibiting delayed failure leading to thermal degradation.

3.3. Heating of the diamond table

In order to gain additional insight into the nature of thermally induced damage, heating experiments were performed on coarse-grained compacts which had the carbide substrate removed in two ways. In one case the entire compact was leached for several days in an HF/HNO_3 solution, which removed not only the carbide but most of the metallic constituents, primarily cobalt, in the diamond layer. In the second case, the carbide was removed by grinding. These specimens were then heated to 900 to 960° C. The uncertainty of the exact temperature was due to the inability to attach a thermocouple to the diamond table; therefore, a sheathed thermocouple was brought into contact with the diamond surface and its temperature recorded. Although calibration tests on a steel specimen showed close correspondence between the contact thermocouple and thermocouples welded to the steel surface, the different nature of the diamond surface made such a calibration open to question. Each test, however, was conducted at the same apparent temperature with a freshly sanded sheathed tip, so although the actual temperature was in doubt, the temperature between specimens was the same.

The major difference between the machined and leached diamond layers was that the former exhibited delayed failure and the latter did not. This is shown in Fig. 11, where the top figure is the event-time plot for the machined layer and the bottom is of the leached one. Although not all the carbide could be removed from the machined diamond layer because it distorted due to residual stresses, most of the effect is thought to be due to the interstitial metal. The significance of this different behaviour will be discussed in Section 4.

3.4. Optical microscopy

Six coarse-grained compacts were chosen for examination by optical microscopy, ranging from those whose wear rates were low to those with high wear rates. The selected drill blanks were wire electro-discharged machined across the diameter of the blank.

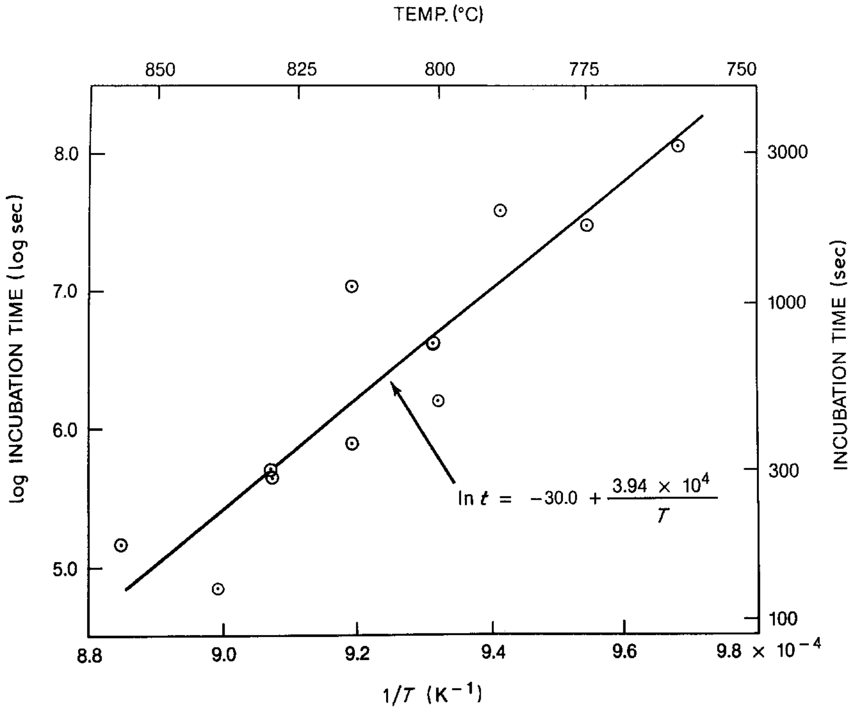

Figure 7 Initiation of delayed failure plotted against reciprocal temperature. $Q = 327\,\mathrm{kJ\,mol^{-1}}$.

Polishing was performed using a rotating diamond compact with water as a coolant. Two compact halves were polished at a time, and were mounted so that the two diamond layers were in contact. In this way, rounding off at the diamond/carbide interface was minimized.

Polished metallographic sections are shown in Figs 12 to 15. Fig. 12 shows both an undamaged blank and a thermally damaged one. While some pull-out of metallic constituents is evident in the undamaged compact, clearly the diamond grains are intact and do not exhibit microcracking. The thermally degraded compact, on the other hand, shows gross intercrystalline fracture, together with transcrystalline cracks. This severe degree of thermal degradation is depicted again in Fig. 13. All compacts exhibiting such microstructures wore rapidly in rock cutting tests.

Figs 14 and 15 are of considerable interest because of their implication to the progression of thermally induced damage. The circumference of the compact shown in Fig. 14 is almost totally destroyed, while for the one displayed in Fig. 15 intergranular cracking is just beginning at the specimen periphery. The amount of damage in the compact shown in Fig. 15 was not sufficiently large to adversely affect the wear of the compact ($6.30 \times 10^{-11}\,\mathrm{cm^3\,cm^{-1}}$), but the damage in the other compact lead to a high wear rate ($2.02 \times 10^{-8}\,\mathrm{cm^3\,cm^{-1}}$). These two micrographs suggest that thermal damage initiates intergranularly at the circumference and then propagates inwards as mixed-mode cracking. This inference is not unreasonable; cracking is generally first noted at the circumference when diamond compacts are overheated.

4. Discussion

As a result of the experimental work conducted during this investigation, additional knowledge regarding the mechanisms of sintered diamond compact thermal damage has been gained. Specifically, the observation of a delayed failure phenomenon which is governed by an Arrhenius relation has implications regarding failure mechanisms. We believe the existence of such a chemically controlled effect, coupled with its absence when most, but not all, of the metallic constituents are removed by leaching, is evidence of diamond graphitization nucleated by the interstitial cobalt and perhaps other minor metallic elements. It should be noted that the initiation of acoustic emission is about the same for the unleached and leached diamond tables (see Fig. 11). However, the leached diamond table emitted only ~290 events, while the unleached one emitted ~2400 events. Based on the correlation

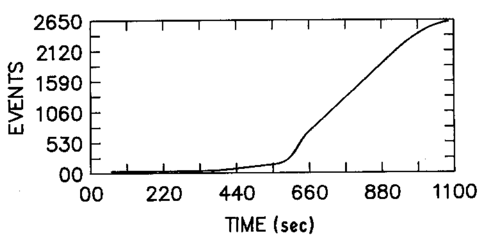

Figure 8 Delayed failure behaviour of a fine-grained drill blank heated at 850° C.

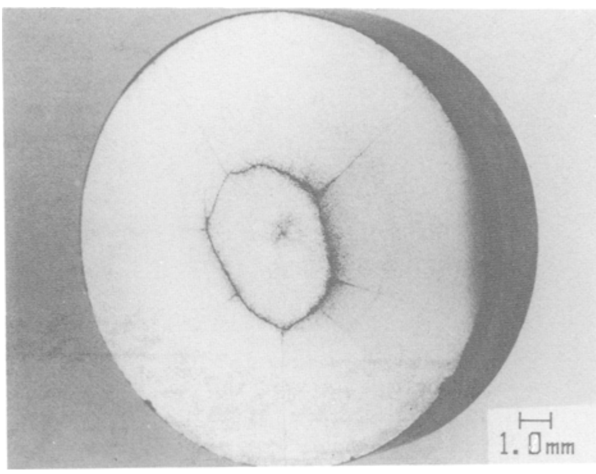

Figure 9 Fracture pattern for a fine-grained drill blank heated for a short time.

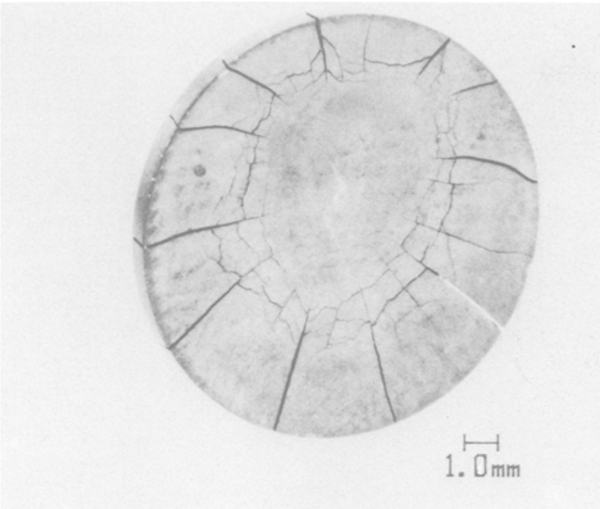

Figure 10 Fracture pattern for a fine-grained drill blank heated for a long time. The diamond table spalled off the carbide substrate.

of wear and acoustic events, the latter material would be considered thermally degraded, and the former not. We suggest a possible mechanism to account for this behaviour in both cases graphitization begins at about the same time, but for the unleached material, cobalt (as well as the diamond-to-graphite volume change) was available to expand and fracture the weakened diamond network. For the leached case, fewer nucleation sites were present (some metallic elements were not removed in spite of acid leaching) and there was only the diamond-to-graphite volume change to disrupt the diamond structure. The identification of graphitization as the primary cause for thermal degradation of diamond compacts has been previously advanced by others [5], and Vornov *et al.* [6] have shown that metallic constituents are necessary for diamond-to-graphite conversion in the temperature range 850 to 1000° C. We feel the present investigation has contributed to this interpretation by showing the time-dependent nature of this damage, which suggests that graphitization must first begin before thermal damage, by whatever means, causes the diamond structure to break-up. It may be noted, parenthetically, that the detection of the initiation of microcracking without a passive measurement system such as acoustic

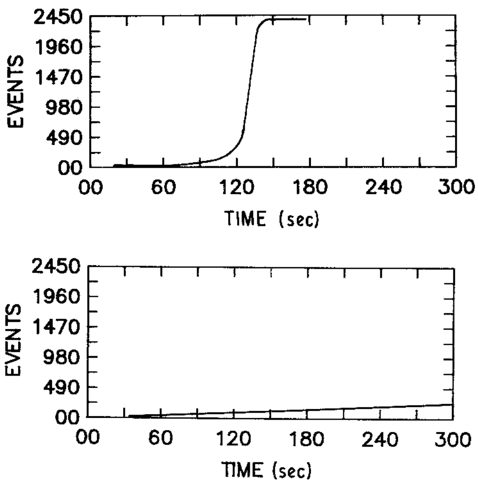

Figure 11 Event–time histories of two diamond layers heated to 900 to 960° C and held at temperature. Top figure, carbide removed by machining, bottom figure, carbide removed by leaching.

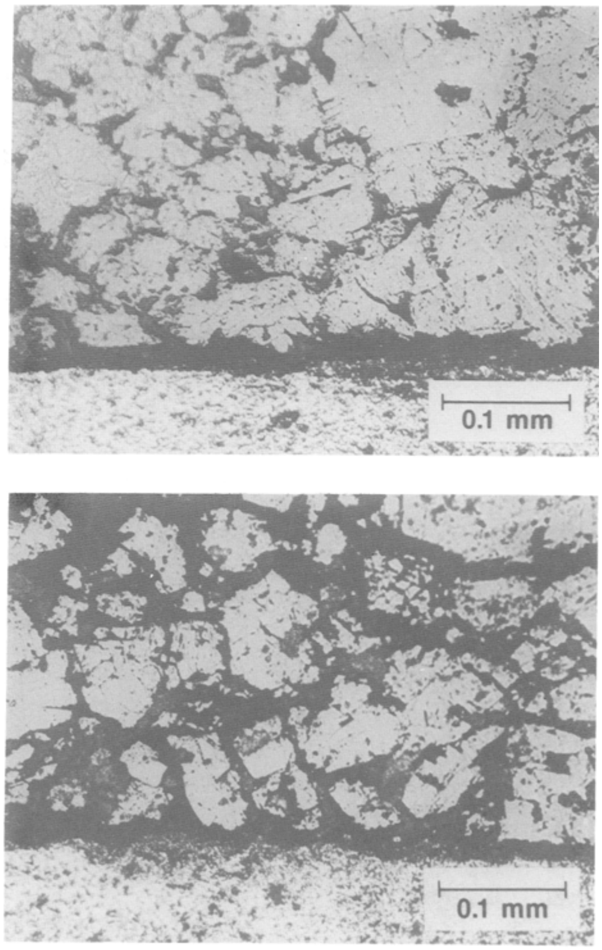

Figure 12 Micrographs of an undamaged diamond compact (top photograph) and one that has been thermally degraded.

emission would require the heating and destructive testing (by wear measurements, metallography, etc.) of an inordinately large number of individual diamond compacts.

The major argument against attributing the experimentally observed Arrhenius relation to initiation of graphitization is the low activation energy for the process compared with that measured for diamond in vacuum. As indicated before, we feel the presence of the metallic phase in the sintered diamond product acts as a catalyst for the graphitization, hence lowering the activation energy. This is additional verification that graphitization occurs at these temperatures and times in sintered diamond compacts. Fig. 16 shows the diamond interface side of a normal (i.e. not overheated) sintered diamond compact, which had the tungsten carbide substrate removed by leaching in an HF/HNO_3 solution. Small diamonds, formed during compact fabrication, are clearly visible. A similar compact was deliberately overheated at a time and temperature known to induce thermal degradation, and the carbide substrate was removed in a similar manner. This diamond compact interface is shown in Fig. 17, and clearly the small diamonds are not present. Their absence after a deliberate excessive heat treatment at the temperatures under consideration ($\sim$ 800 to 900° C) confirms that graphitization in diamond compacts can occur and supports the identification of the Arrhenius relation with graphitization.

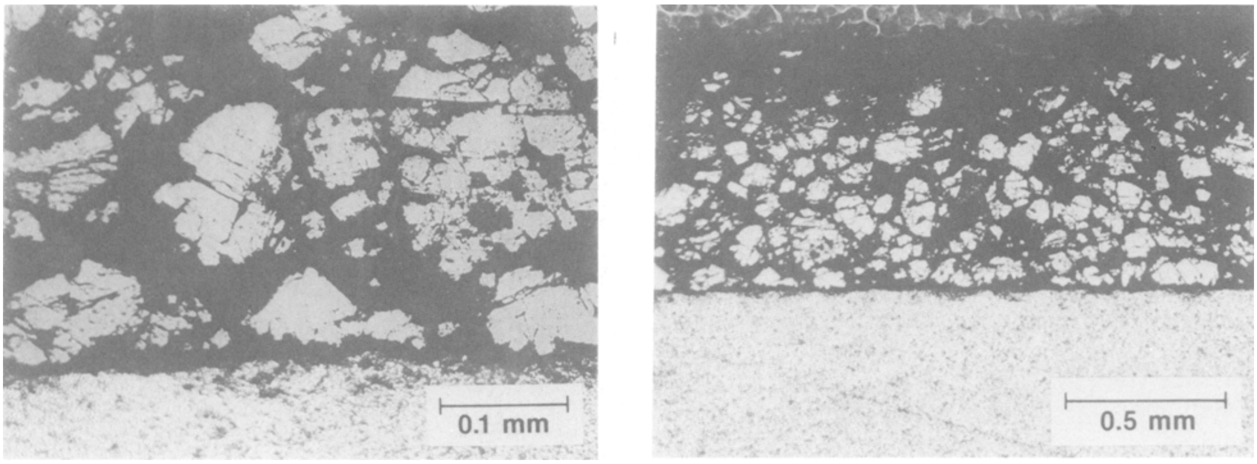

Figure 13 Badly degraded diamond compact at high and low magnification.

5. Conclusions

Under the experimental conditions employed in this investigation, several conclusions may be drawn regarding the behaviour of coarse- and fine-grained polycrystalline diamond compact drill blanks after being subjected to a heating cycle. It should be emphasized that these conclusions regarding thermal degradation are based on data obtained under closely controlled laboratory conditions not generally realized in practice, and due care should be taken in applying these data to service conditions.

1. Sintered diamond compacts undergo a delayed failure phenomenon at temperatures of about 870° C and lower (the existence of a lower limit was not explored). At these temperatures, the compacts behaved normally while being held at temperature, and then after an incubation time they began to thermally degrade, as detected by acoustic emission and confirmed by wear tests. Lower temperatures lead to longer incubation times.

2. The temperature dependence of the delayed failure time for the coarse-grained compacts obeyed

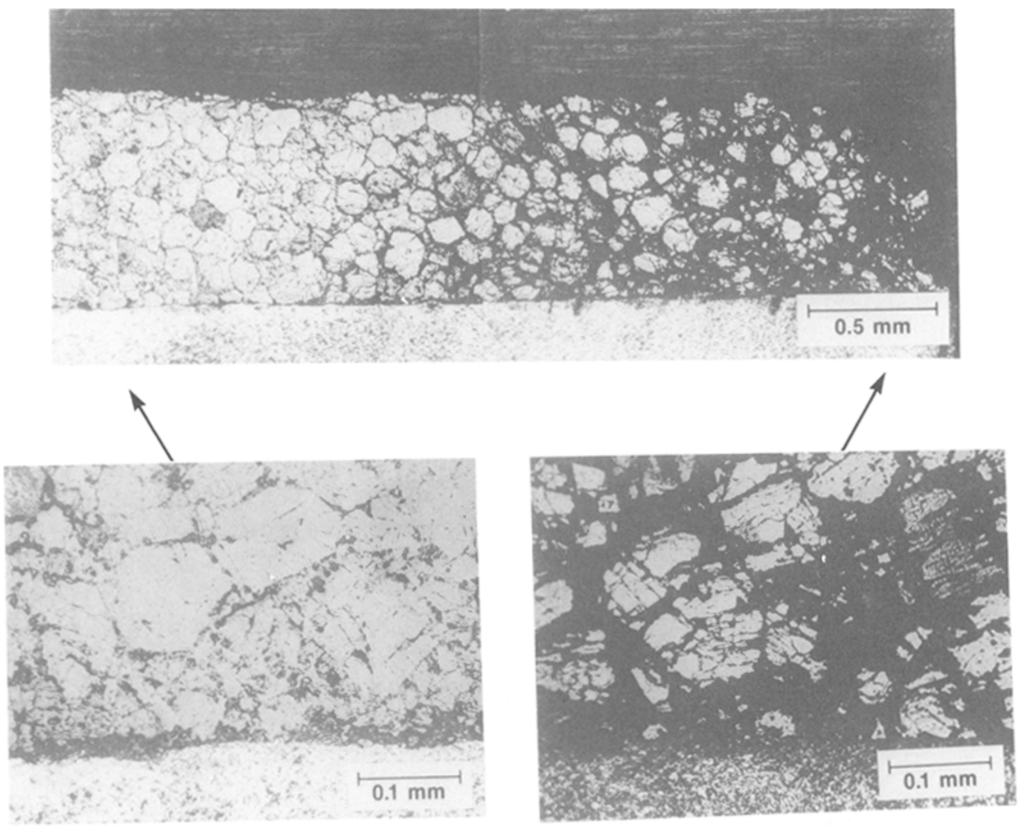

Figure 14 Cross-section of a diamond compact showing severe thermal damage at the specimen periphery.

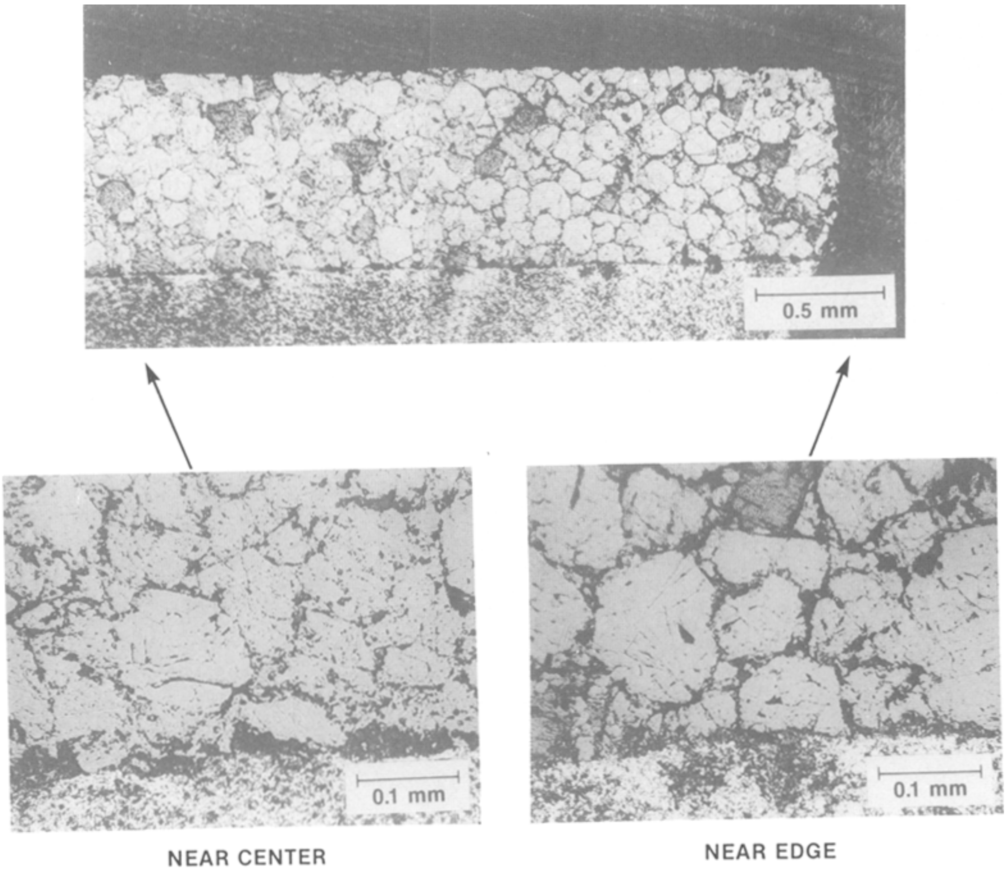

Figure 15 Cross-section of a diamond compact just beginning to exhibit intergranular cracking at the periphery.

an Arrhenius relation with an activation energy of 327 kJ mol^{-1}. This behaviour is attributed to graphitization.

3. Coarse-grained diamond tables with the carbide substrate removed by machining exhibited the same delayed failure phenomenon, but leached diamond tables did not.

4. Fine-grained compact drill blanks failed in a different manner. Under short-term heating tests, failure occurred suddenly and catastrophically with the fracture pattern consisting of several radial cracks terminating in an interior circumferential crack. The fracture was more energetic, emitting a larger amount of acoustic events. These blanks also exhibited delayed failure, but at a somewhat higher temperature.

5. Metallographic examination of degraded and nondegraded coarse-grained compact cross-sections indicated that initially failure occurred intergranularly at the compact periphery. Transgranular cracking then occurred, and the thermally damaged region proceeded inwards.

6. Irrespective of time and temperature, if no more than 400 acoustic events were detected for the coarse-grained compacts, no thermal degradation was

Figure 16 Diamond compact side of the diamond/carbide interface of a normal (not overheated) polycrystalline sintered diamond compact drill blanks with the tungsten carbide substrate removed by acid leaching. Note the presence of small diamonds.

Figure 17 Diamond compact side of the diamond/carbide interface of an overheated polycrystalline sintered diamond compact drill blank with the tungsten carbide substrate removed by acid leaching. Note the absence of small diamonds.

observed based on rock-cutting wear tests. Above 1000 events, degradation was observed. Between 400 and 1000 events, degradation may or may not occur.

Acknowledgements

We thank G. C. Sogoian and G. C. Buczkowski for rock cutting and acoustic emission testing, respectively, and C. R. Morelock for the preparation of the polished diamond compact sections.

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Received 10 February
and accepted 10 June 1988