JOURNAL OF MATERIALS SCIENCE 23 (1988) 3821–3826

Behaviour of cobalt infiltration and abnormal grain growth during sintering of diamond on cobalt substrate

SHI-MING HONG*, MINORU AKAISHI, HISAO KANDA, TOSHIKAZU OSAWA, SHINOBU YAMAOKA
National Institute for Research in Inorganic Materials, Namiki 1-1, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

OSAMU FUKUNAGA
Department of Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguroku, Tokyo 152, Japan

The infiltration behaviour of molten cobalt into a diamond powder compact was examined when the latter was placed on a cobalt disc and held at high pressure of 5.8 GPa and high temperature of 1350 to 1500° C. The larger the grain size of the starting diamond powder and the higher the holding temperature, the more easily cobalt infiltrated into the diamond compact. The infiltration is considered to occur because of the negative pressure in the voids formed between diamond grains. Although diamond powder was consolidated in this process of cobalt infiltration, abnormal grain growth was also observed in the boundary between cobalt and diamond compact because of the dissolution and precipitation process of the compact into molten cobalt.

1. Introduction

Sintered diamond compacts are highly abrasive materials which can be used as wire drawing dies, rock-drilling bits and cutting tools for non-ferrous metals and ceramics. In making them, it is known that cobalt plays an important role as a binder or sintering aid [1–6].

In the sintering of the diamond–cobalt system at high pressure and high temperature, two methods have been adopted. One is that in which a powder mixture of diamond and cobalt is used as a starting material and consolidated to form a diamond compact [1–3]. The other is that in which pure diamond powder is placed on the substrate of cemented tungsten carbide with cobalt binder (WC–Co), and consolidated *in situ* on the substrate [4–6]. The diamond compact made by the latter method is easy to solder because it has a WC–Co substrate which is very useful when it is actually used as a tool.

In making a diamond compact by the latter method, the cobalt in the WC–Co substrate infiltrates into the diamond particles and serves as an agent for forming diamond–diamond direct bonding. Therefore, for the purpose of understanding the sintering mechanism, it is very important to make clear the behaviour of cobalt infiltration. However, there have been no reports from this point of view. In this context, as a model experiment of cobalt infiltration, high temperature and high pressure experiments were carried out by placing diamond powder on a cobalt disc instead of a WC–Co disc, and the effects of temperature and the original grain size of the diamond on the behaviour of cobalt infiltration were examined.

Abnormal grain growth of diamond was observed in the boundary between the diamond compact and cobalt disc throughout the experiments. As this phenomenon is not only interesting but also important as a sintering control, it was also examined.

2. Experimental procedures

The experiment was carried out using a modified belt type high pressure apparatus with 25 mm bore diameter the same as that reported by Akaishi *et al.* [2]. The sample configuration is shown in Fig. 1. As the starting material, three kinds of synthetic diamond powder with grain size of 0 to 1 μm, 5 to 10 μm and 20

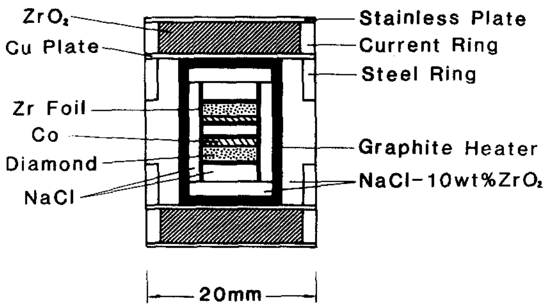

Figure 1 Sample configuration for high pressure and high temperature experiments.

---

*On leave from Chengdu University of Science and Technology, Chengdu, China.

0022-2461/88 $03.00 + .12 © *1988 Chapman and Hall Ltd.*

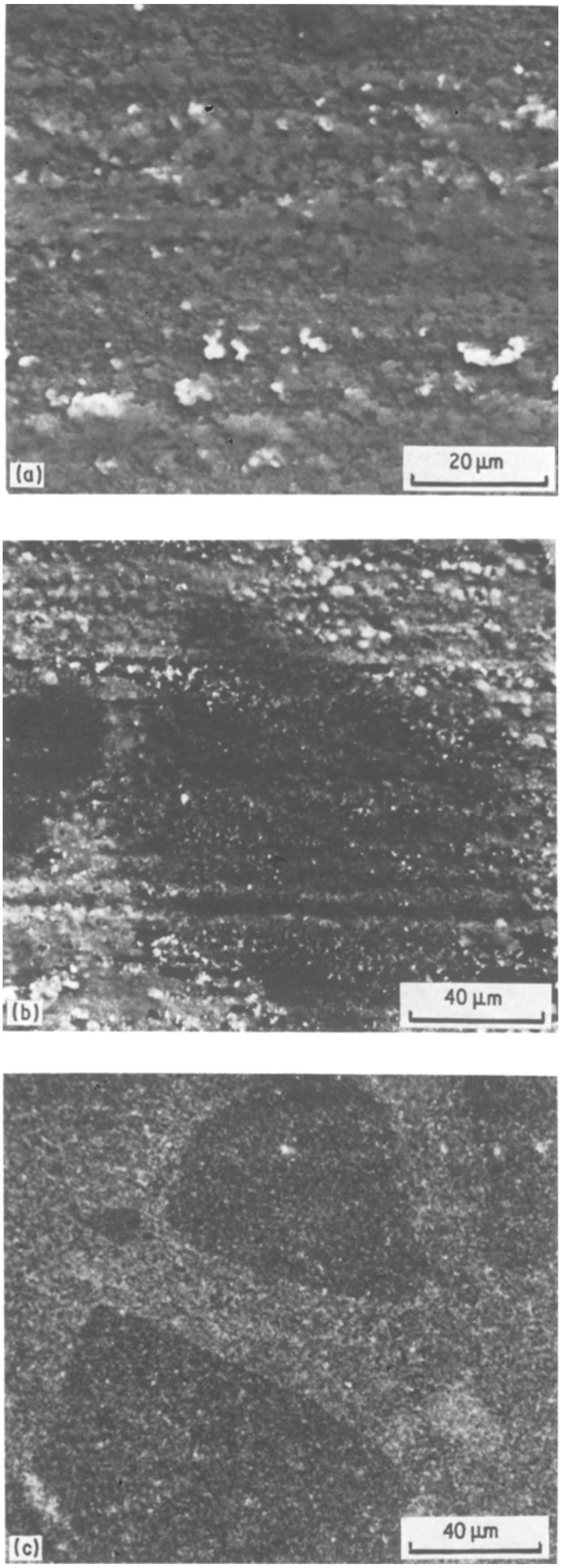

Figure 2 BEI micrographs of the polished section in a diamond layer. (a) sample A, (b) sample B and (c) sample C.

to 30 μm (obtained from Tomei Diamond Co.) and cobalt disc with 99.9% purity were used.

Samples were first compressed to a pressure of 5.8 GPa, then heated to a temperature between 1350 and 1500° C, held for 10 to 360 min, cooled to room temperature and finally decompressed. Temperature was estimated from the predetermined relation between input electrical power and Pt6% Rh–Pt30% Rh thermocouple e.m.f. at 5.8 GPa using a similar sample configuration. The pressure effect on the thermocouple e.m.f. was not corrected. Pressure was determined by using the known transitions of

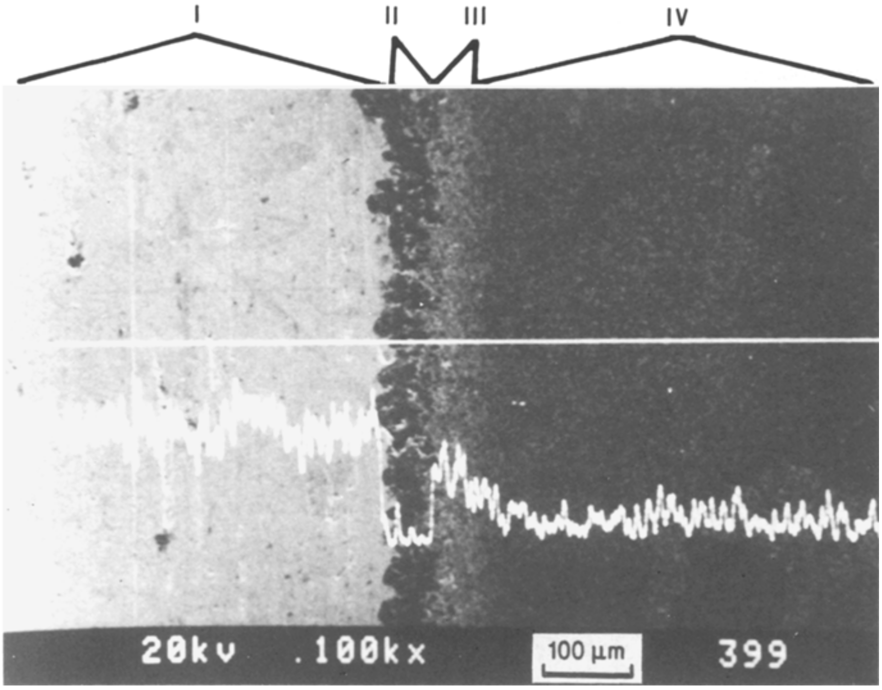

Figure 3 Distribution of cobalt concentration along the line in the polished section of sample F (Co Kα by EDX).

bismuth (2.5 GPa), thallium (3.6 GPa) and barium (5.5 GPa).

All the experiments were carried out at a pressure of 5.8 GPa. The holding temperature was chosen in such a way that a sample should be above the eutectic temperature of the diamond–Co system in the diamond stable region. It is known to be about 1336° C at 5.6 GPa [7]. Thus a temperature range of 1350 to 1500° C was chosen for this study. The starting materials and their sintering conditions are listed in Table I.

The obtained samples were cut and polished, or fractured, and then, if necessary, these polished or fractured samples were treated by hot hydrochloric acid to remove cobalt on the surface. The surface was observed through an optical microscope, a secondary electron image (SEI) or backscattered electron image (BEI) of a scanning electron microscope and an energy dispersive X-ray micro-analyser (EDX).

3. Results and discussion

3.1. Behaviour of cobalt infiltration into diamond layer

It was found that cobalt infiltrated into the diamond layer to a greater or lesser degree in all the experiments. There was no difference in the cobalt infiltration between the upper and lower samples in Fig. 1. This means that it is not influenced by gravity.

TABLE I Starting materials and sintering conditions

Run	Starting diamond grain size (μm)	Holding temperature (° C)	Holding time (min)
A	0–1	1350	60
B	0–1	1375	60
C	0–1	1400	60
D	5–10	1350	60
E	5–10	1400	60
F	5–10	1450	60
G	5–10	1500	60
H	20–30	1350	60
I	20–30	1400	60
J	5–10	1450	10
K	5–10	1450	360

Fig. 2 shows the BEI of samples A, B and C listed in Table I, where the starting diamond particles were very fine (less than 1 μm) and the holding time was 60 min. From the figure it can be observed that in sample A, held at 1350° C, the cobalt was scattered in the diamond layer and its content was very small (Fig. 2a). In samples B and C held at 1375 and 1400° C, respectively, the cobalt content increased in a heterogeneous distribution. As shown in Figs 2b and c, many small dark areas of about several tens to a few hundreds of micrometres across could be seen. As this area was darker in the BEI, it can be said that there was less cobalt in this area. The boundary of this area became vague in sample C, showing that the cobalt content increased at higher holding temperature even in this area.

This phenomenon can be explained as follows. At 1350° C, very little cobalt can infiltrate, but at higher temperatures much more can infiltrate. On the other hand, very fine powdered diamond tends to form agglomerates of about several tens to a few hundreds of micrometres in size and usually they are densely compacted. When cobalt infiltrates into the diamond layer, it is difficult to infiltrate into the agglomerates. Then, heterogeneous cobalt distribution occurs. However, at higher temperature, cobalt can infiltrate even into the area of agglomerates and the heterogeneity decreases. This phenomenon is very important when it is intended to make a homogeneous diamond compact with small grain size.

On the other hand, in the samples from D to I with fairly large grain size of 5 to 10 μm and 20 to 30 μm, cobalt infiltrated homogeneously throughout the diamond layer with a thickness of about 2 mm, and sometimes a thin cobalt layer of several tens of micrometres was formed on the end surface of the diamond layer.

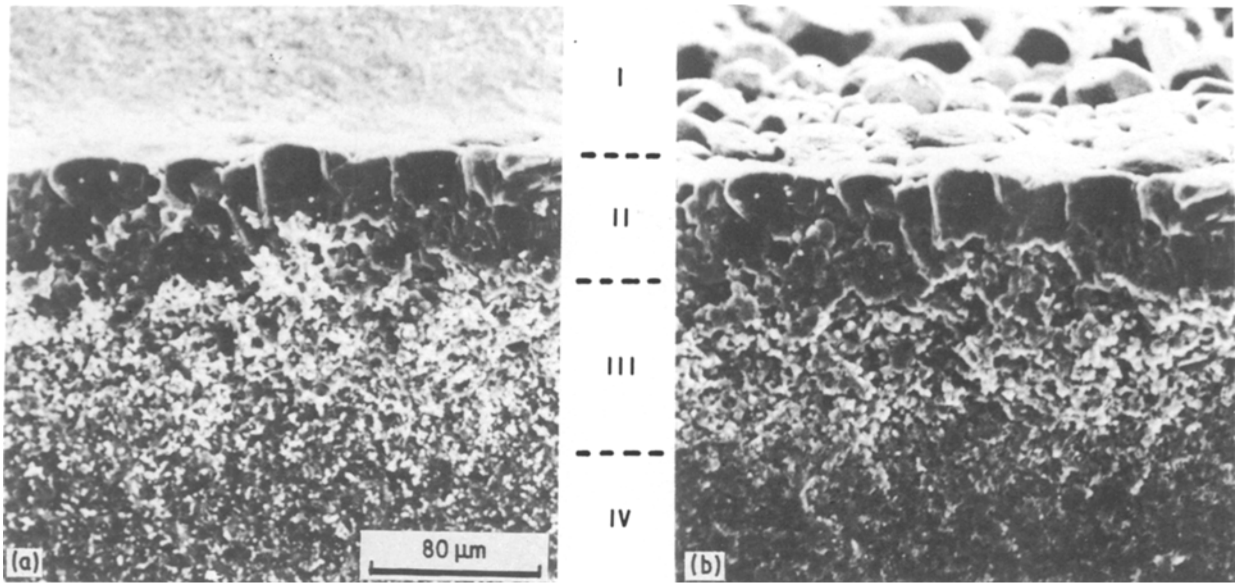

Figure 4 SEI micrographs of sample F (a) before and (b) after acid treatment.

To discuss the effect of grain size on cobalt infiltration, the experiments of A, D and H at the same holding temperature of 1350° C are compared. In run A with grain size of 0 to 1 μm, the cobalt content in the diamond layer was very small and the distribution was not homogeneous. In runs D and H with a grain size of 5 to 10 μm and 20 to 30 μm, respectively, cobalt content was much larger and the distribution was homogeneous. Consequently, it can be said that at the same temperature the larger the grain size, the more easily cobalt can infiltrate into the diamond layer.

These experimental results can be explained by

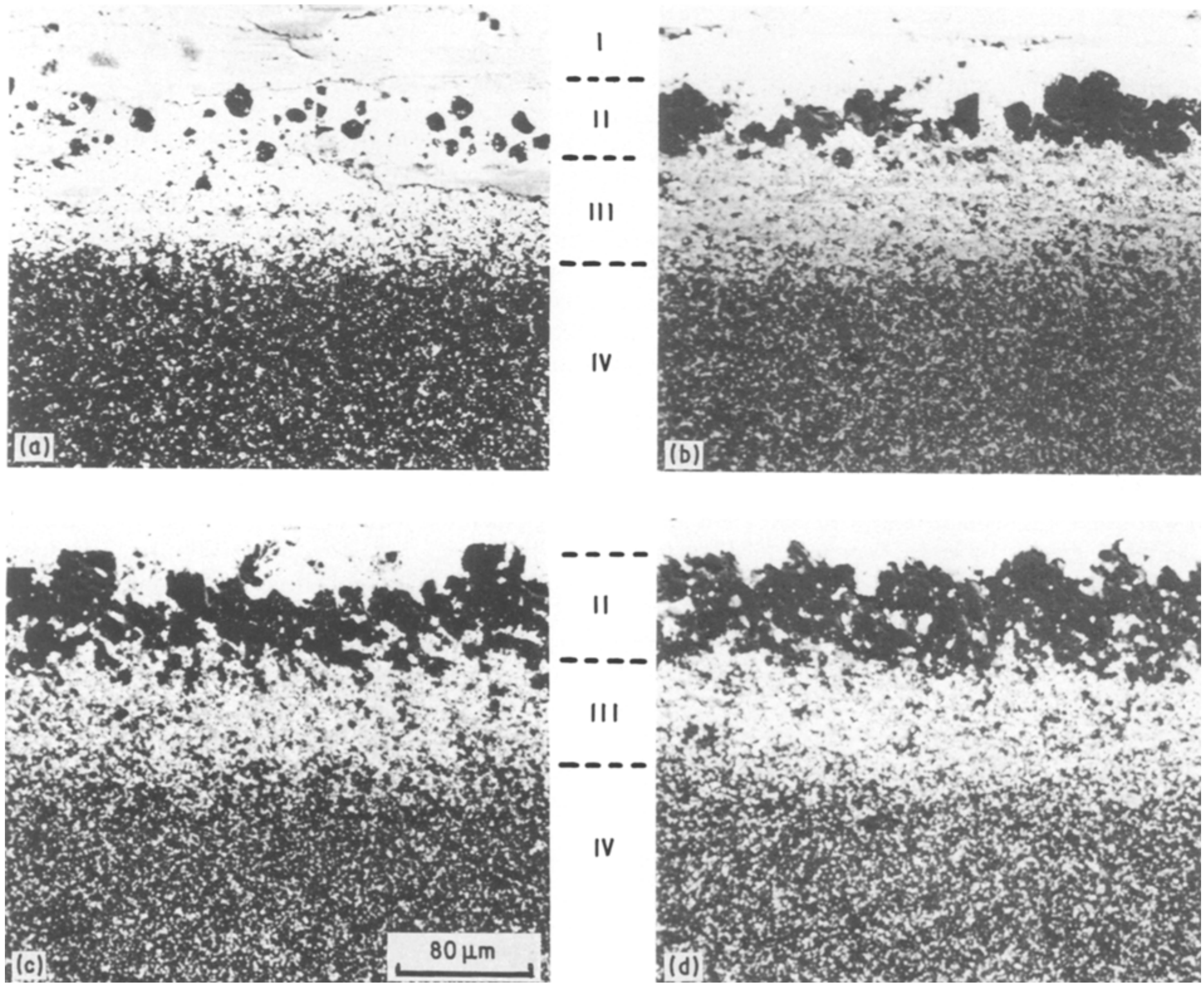

Figure 5 BEI micrographs of the polished sections. (a) sample D, (b) sample E, (c) sample F and (d) sample G.

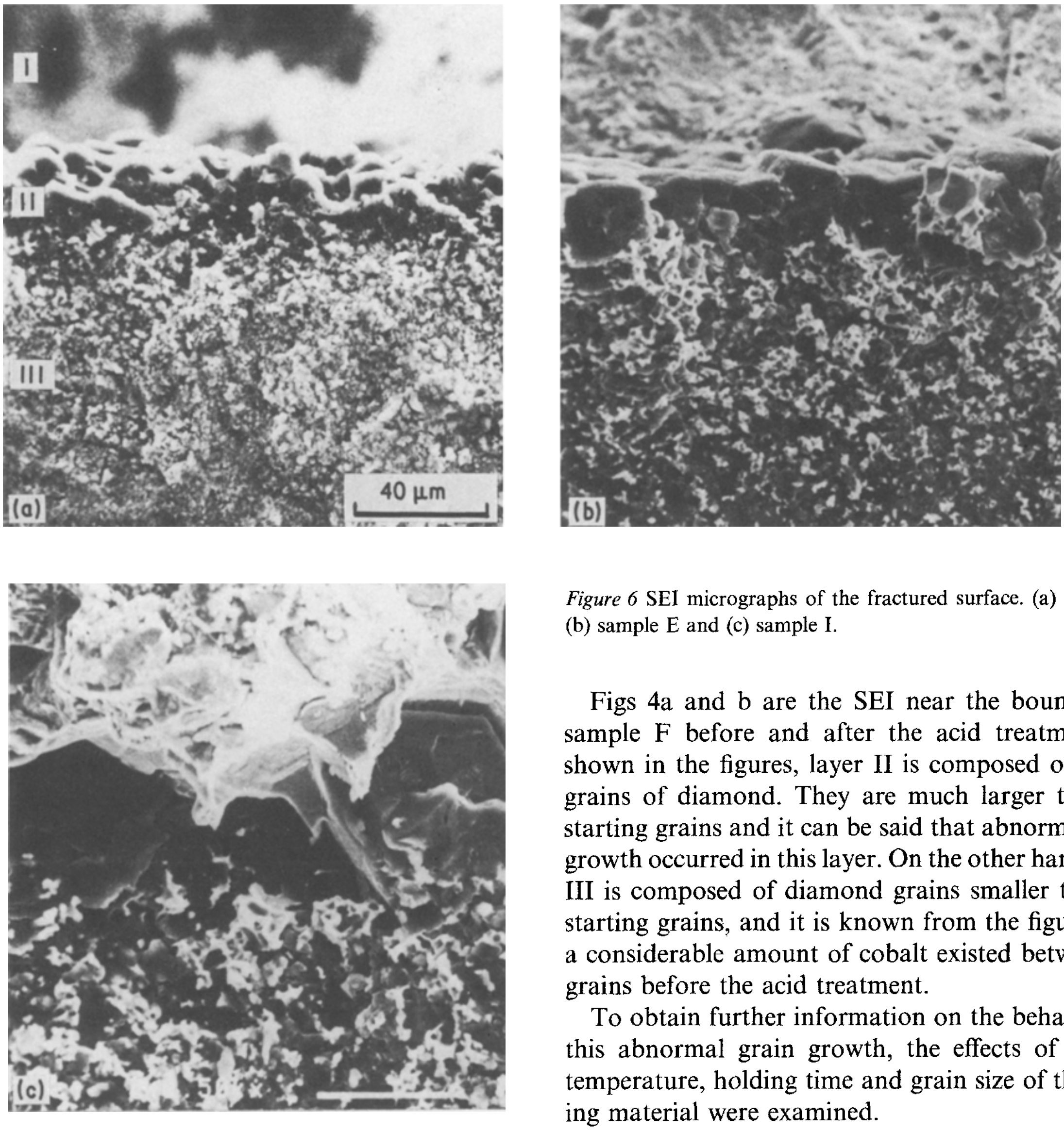

Figure 6 SEI micrographs of the fractured surface. (a) sample C, (b) sample E and (c) sample I.

considering the following two factors. One is the voids formed between the grains in the diamond layer. The pressure in the voids must be much lower than that in the grains. Therefore, molten cobalt is considered to be sucked into the diamond layer through the voids. Besides, the size of the voids becomes larger when the grain size is large, and the larger the size, the more easily cobalt can move. The other factor is the viscosity of the molten cobalt which becomes lower when the temperature increases. Of course, the lower the viscosity, the more easily cobalt can move. This is the reason why cobalt can infiltrate more easily at higher temperature and when diamond powder of a larger grain size is used.

3.2. Abnormal grain growth in the boundary

In order to know the distribution of the cobalt content in the diamond layer, a line analysis of Co Kα in EDX was done along the polished section of the present samples. Fig. 3 shows the distribution of cobalt concentration in run F. As shown in the figure, layers with little cobalt (II) and with a lot of cobalt (III) were present between the two layers of cobalt (I) and diamond compact (IV). In the layer IV, cobalt content was nearly constant.

Figs 4a and b are the SEI near the boundary of sample F before and after the acid treatment. As shown in the figures, layer II is composed of coarse grains of diamond. They are much larger than the starting grains and it can be said that abnormal grain growth occurred in this layer. On the other hand, layer III is composed of diamond grains smaller than the starting grains, and it is known from the figures that a considerable amount of cobalt existed between the grains before the acid treatment.

To obtain further information on the behaviour of this abnormal grain growth, the effects of holding temperature, holding time and grain size of the starting material were examined.

From the sample observation of runs J, F and K in which only the holding time was changed, it was found that the abnormal grain size increased with time. The average grain size was about 20 μm, 50 μm and 90 μm in the samples J (10 min), F (1 h) and K (6 h), respectively, where the numbers in parentheses are the holding times. The thickness of layer II also increased with time. Particularly, in run K, abnormal grain growth prevailed all over the diamond.

From the sample observation of runs D, E, F and G in which only the holding temperature was changed, it was found that both the thickness of layer II and the abnormal grain size increased with temperature. Figs 5a, b, c and d are the BEI of the sections of samples D, E, F and G, respectively. In sample D, held at 1350° C, small numbers of dispersed abnormal grains were seen (Fig. 5a). In sample E, held at 1400° C, the number of the grains increased and were connected to one another (Fig. 5b). In samples F and G held at 1450° C and 1500° C respectively, this tendency increased and the average thickness of the layer became about 70 μm and 80 μm, respectively (Figs 5c and d). This result shows that the rate of abnormal grain growth increases with temperature. It must be noted that the thickness of layer III remained almost constant over the four experiments.

The effect of the starting grain size was examined

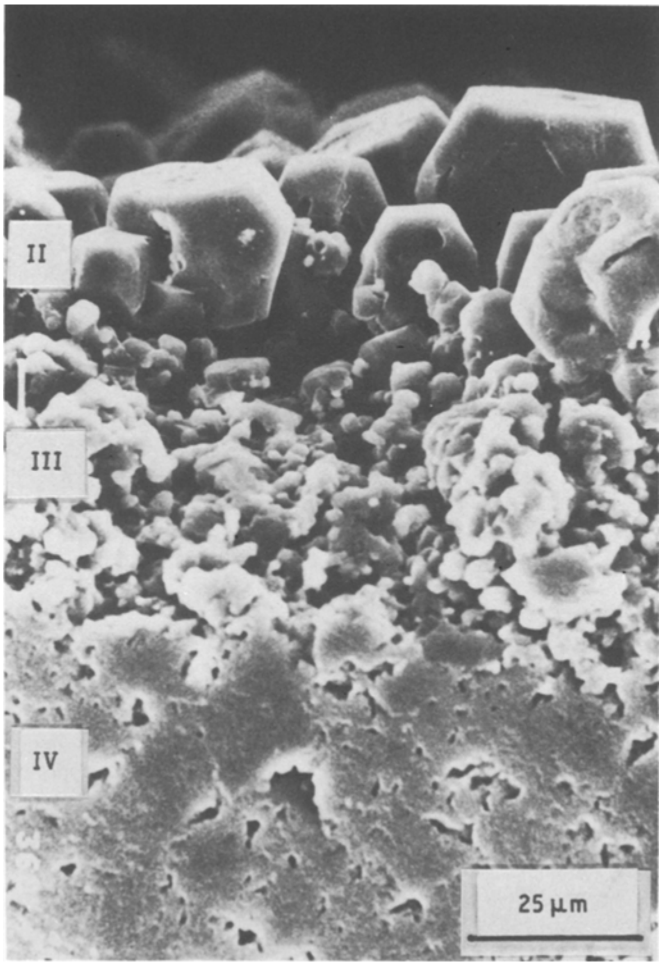

Figure 7 SEI micrographs of the polished section of sample H after acid treatment.

from a comparison of runs C, E and I. Figs 6a, b and c show SEI of the fractured surface of the samples of C (0 to 1), E (5 to 10) and I (20 to 30), respectively, where the numbers in the parentheses are the starting grain size in micrometres. From the figure it was found that the size of abnormal grain increased with increasing the starting grain size. That is, the average grain size was about 10 μm in sample C, 30 μm in E and 60 μm in I. However, the ratio of the size of abnormal grains to that of the starting ones decreased with increasing starting grain size. The thickness of layer III increased with the decrease of the size of starting grains. They were about 100 μm, 80 μm and 60 μm in samples C, E and I, respectively.

Sometimes cobalt accumulated at the opposite end of the diamond layer. Abnormal grain growth was also observed in this boundary. It means that this phenomenon occurs in the region where cobalt is high in concentration.

Based on experimental results obtained in the present study, the abnormal grain growth can be explained by the recrystallization process of the dissolution and precipitation of the sintered diamond into the molten cobalt. Namely, diamond compact was dissolved by molten cobalt in layer III and the large recrystallized diamonds were precipitated in layer II. This explanation is supported by Fig. 7. Fig. 7 is the SEI of the polished section of sample H after acid treatment, where diamond powder with a grain size of 20–30 μm was used as a starting material. The grain size in layer III is much smaller than that in the starting grains, meaning that diamond is dissolved in this region.

It must be noted that this reaction becomes conspicuous when the diamond compact contacts with highly concentrated molten cobalt. Therefore, it is thought that this phenomenon was seen particularly in this model experiment where a pure cobalt disc was used instead of a WC–Co base.

References

1. H. KATZMAN and W. F. LIBBY, *Science* **172** (1971) 1132.
2. M. AKAISHI, H. KANDA, Y. SATO, N. SETAKA, T. OSAWA and O. FUKUNAGA, *J. Mater. Sci.* **17** (1982) 193.
3. Y. NOTU, T. NAKAJIMA and N. KAWAI, *Mater. Res. Bull.* **12** (1977) 1079.
4. R. H. WENTORF and W. A. ROCCO, US Patent 3745623 (1973).
5. *Idem*, US Patent 3767371 (1973).
6. M. AKAISHI, Y. SATO, N. SETAKA, M. TSUTSUMI, T. OSAWA and O. FUKUNAGA, *Amer. Ceram. Soc. Bull.* **62** (1983) 689.
7. H. M. STRONG and R. E. TUFT, "Report No. 74CRD118" (G.E. Research and Development, New York, 1974).

Received 5 October 1987
and accepted 26 January 1988