# Industrial Diamond and Cubic Boron Nitride Synthesis and Application to Ceramics

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Yesterday professor Yanagida mentioned that fine ceramics are difficult in producing production, difficult in machining and difficult in utilization, but create high valuable materials. This phrase can typically convented to the industrial diamond and cubic BN. These materials are difficult in production and difficult in machining, but may be create high valuable commercialized materials. Today's my talk would can centrate industrial production, how to product by industrial scale for these materials. Before I'll mention about the ceramic materials of the diamond and cubic BN, as you know well, these materials can be converted to the ceramics, or more well familier to the form of jewels, abrasive stones and others. In the 1st floor, in this moning, colleagues presented to lectures about thick films, coating on the substrate, and I have mentioned that another application may be whiskers, but nobody does not realize yet. Today's my talk will concentrate about ceramics, how to make diamond ceramics and cubic BN ceramics and how to use to the fine ceramics application. As you know, final process of fine ceramics, especially engineering fine ceramics, it does need machining, grinding, cutting, such kind of treatment. In this circumstances, diamond is best material to cut, grind fine ceramics.

Fig. 1 is the some statistics in Japan how to increase diamond consumption and this is the account of only imported diamonds. Almost of imported diamonds were synthesized and natural diamonds are very small in amount. Fig. 2 shows that wholy industrialized countries consume very large amount of diamonds. For example Japan consumes about 20% of the world's consumption. As shown in Fig. 3 we are using diamond mainly for two purpose. One is cutting and grinding the fine ceramics, and this amount increases very drasticaly. Consumption for others purpose in almost flat. In the past day of this seminar, Dr. Kobayashi mentioned, fine ceramics in Japan, how to be grown in production Fig.4 is increasing production curve of fine ceramics. We need much, much diamond to machine, grind the fine ceramics.

Fig.5 shows typical diamond grains. There are two types of grains. One is very regular in shape and lookes like single crystal. Other one is more irregular in shape and this type of diamond grain is very important to cut and grind fine ceramics. In some cases, we must find out more better diamond grains to cut or grind fine ceramics. Almost these are now used for stone cutting and stone grinding, and these irregular grains are now used for we grinding. Grains at right side of Fig.5, we call metal bonding grains, bonded by metals. Grains at left side are bonded by resin, mainly for we grinding. Almost 99.9% synthetic diamonds are now produced by static high pressure technique. Regenos of pressure and temperature we use are roughly 55K bar and

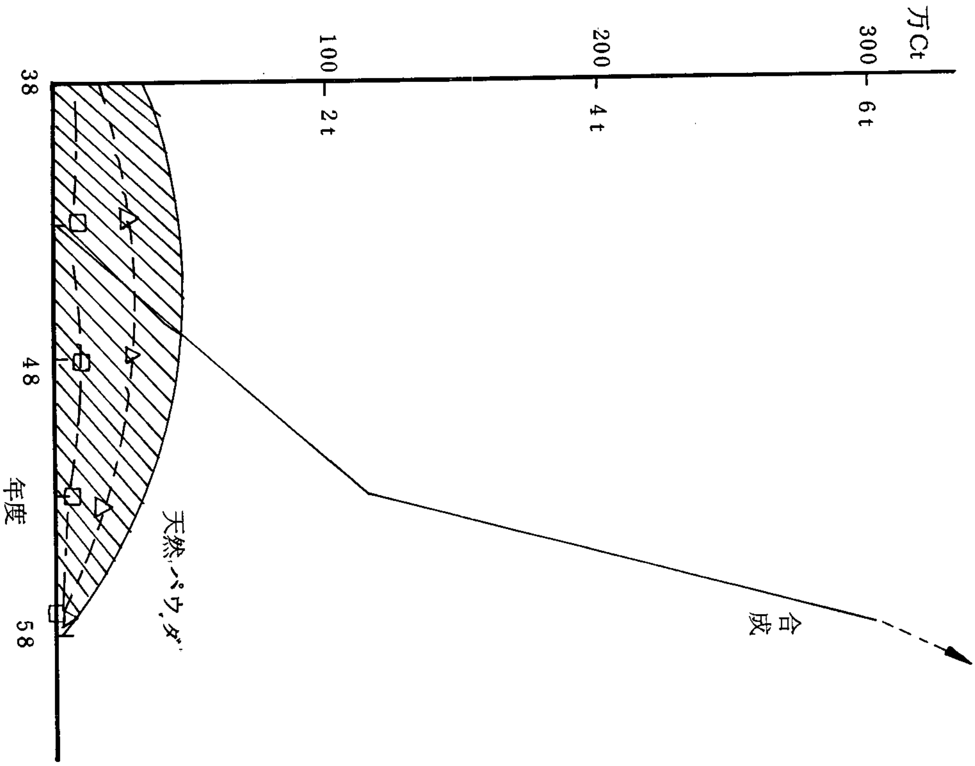



Fig.1 工業ダイヤモンド輸入通關量

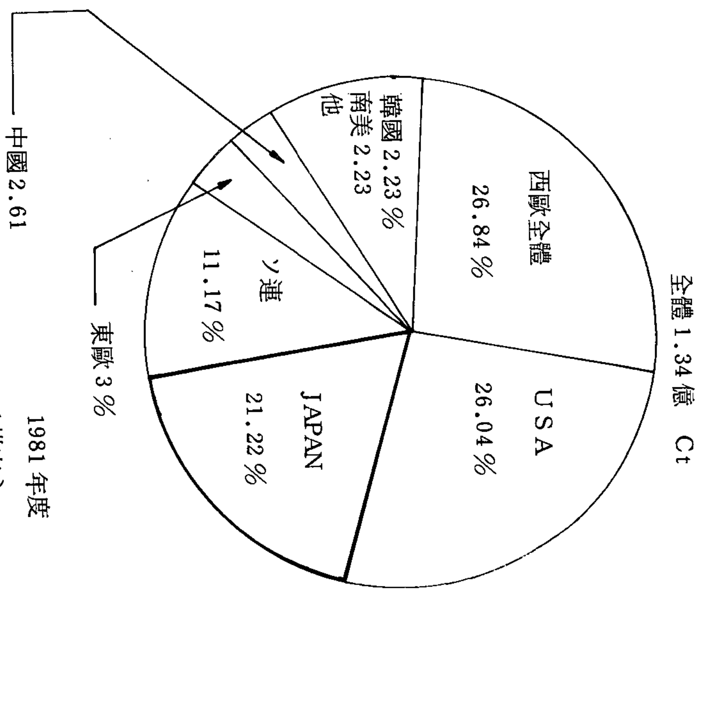



Fig.2 全世界のダイヤモンド消費

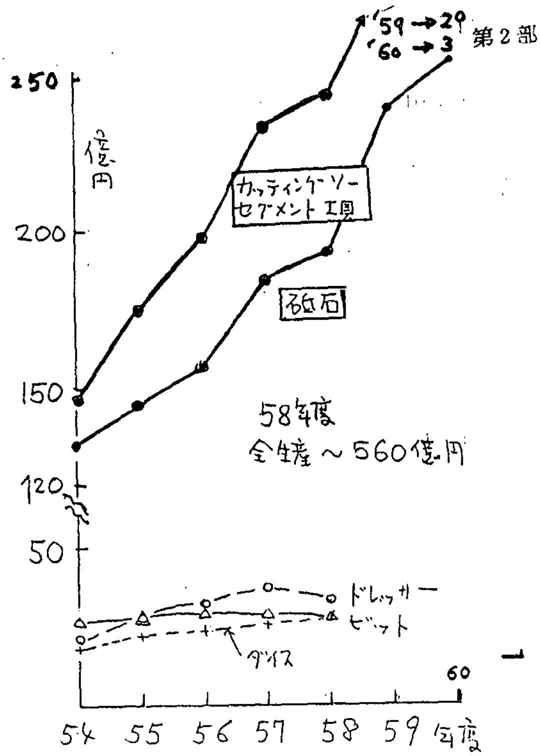



Fig.3　ダイヤモンドの生産額

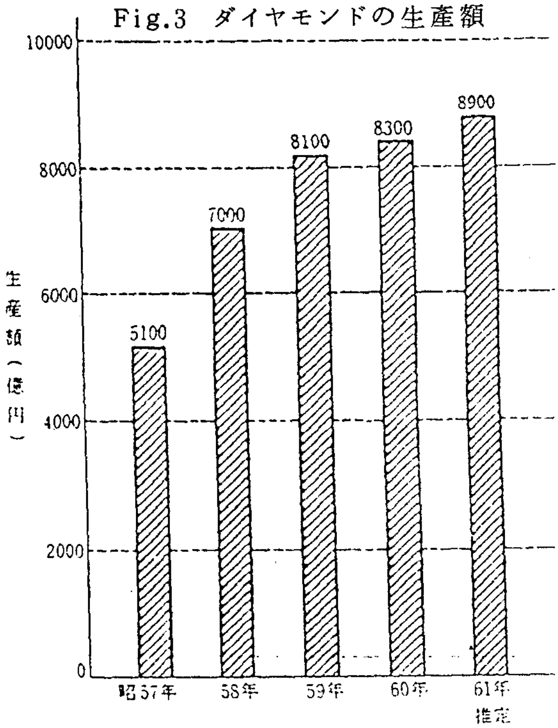


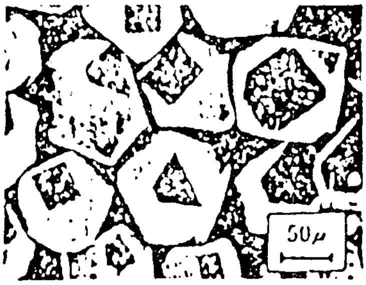

Fig.4　ファインセラミックス部材の年間生産額の推移


(a) G1Nグループ


(b) G2Nグループ


(c) G3Nグループ


(d) NRB1 55N




(e) G6グループ

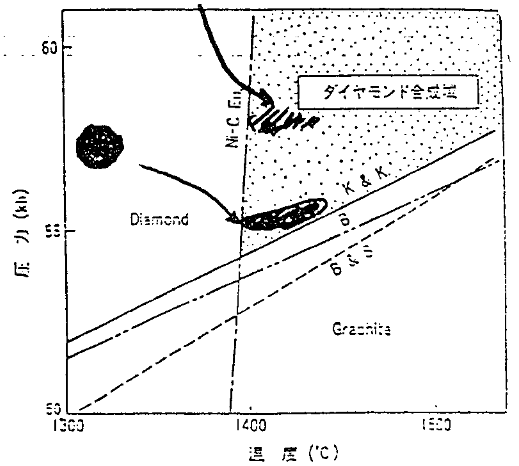

(f) G5グループ


(g) G4グループ


(h) SND-MB

Fig.5 各種ダイヤモンド砥粒（＃140／170）

1400°C as shown in Fig.6. You looked two different grains of diamond in Fig.5 Reogeon, regular grains are synthesized, has very narrow limited temperature range, but irregular grains can be obtained in any other regeons. So irregular grins can be easily produced and regular shaped grains are more difficult. In Fig.7, we can look the regeon of synthesis more largely but the synthetic regeon is little different by the catalyst we use. Normally we use Co - Ni - Fe and it is important catalyst to synthesize diamond from graphite.




Ni-C Eu.: 共融線
- K & K: Kennedy-Kennedy (1976)
B: Bundy et al. (1961)
R & S: Berman-Simon (計算値)

Fig.6 ダイヤモンド／黒鉛平衡線とNi-C共融線

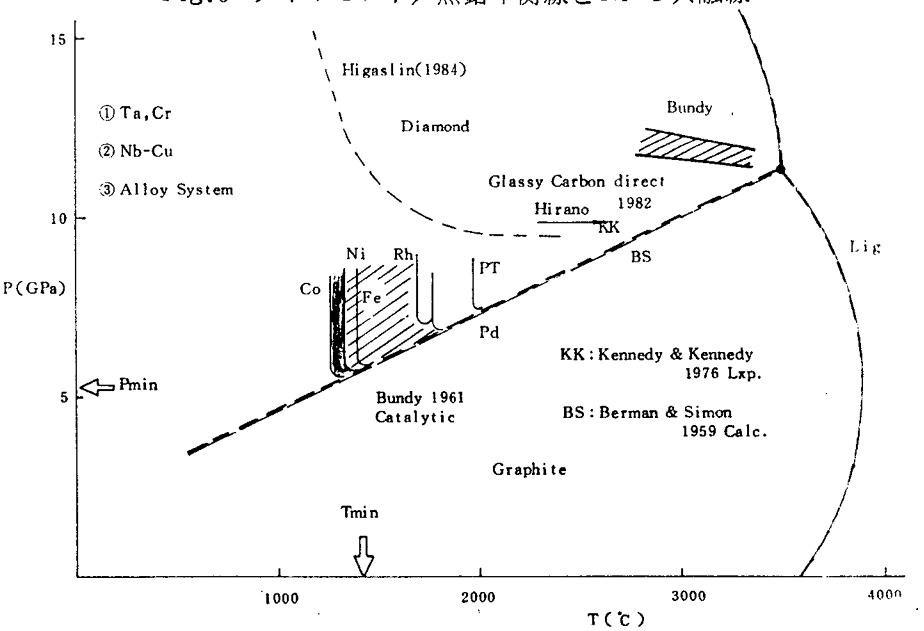



Fig.7 Synthetic Region of Diamond

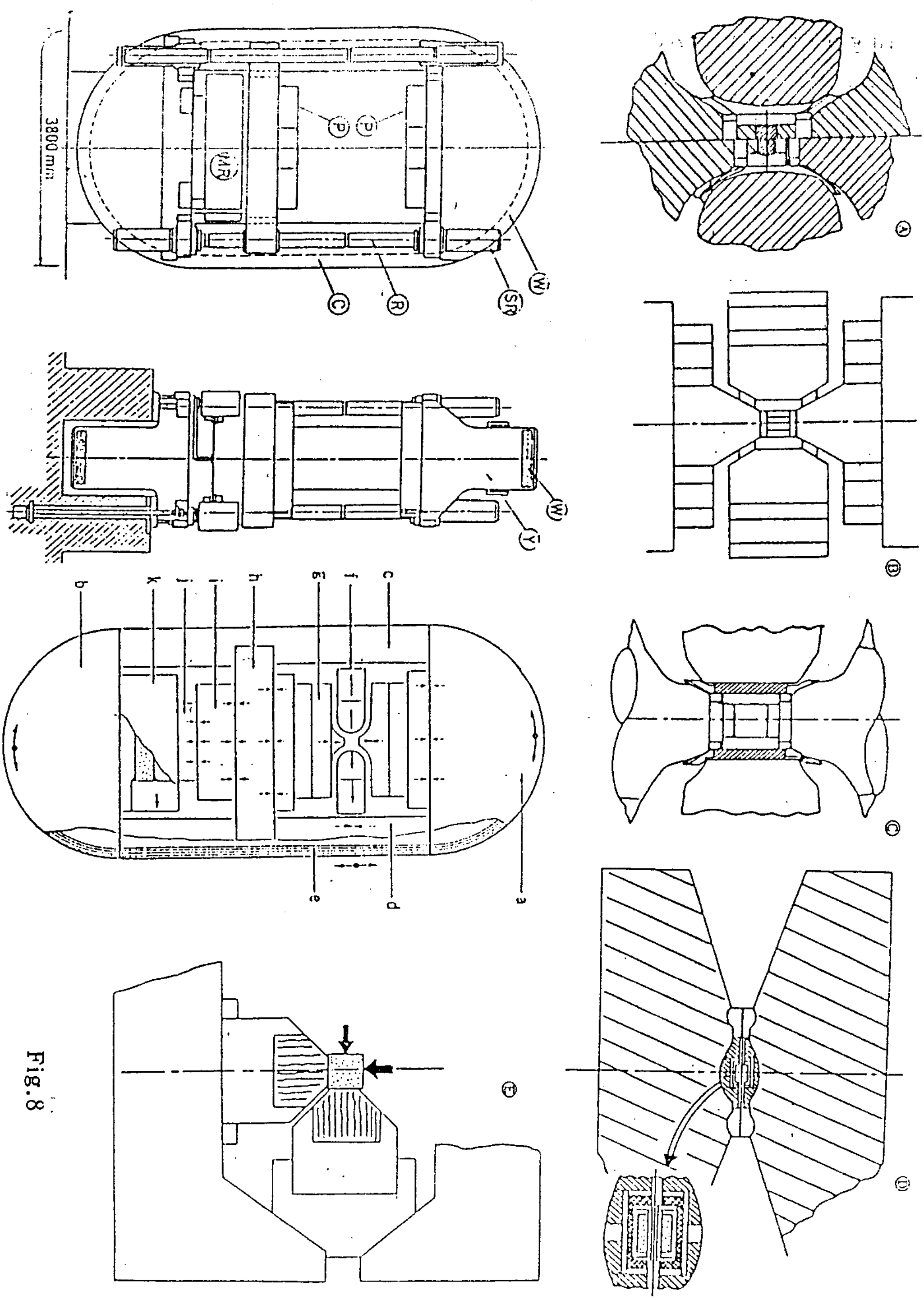



Fig.8

Fig. 8 is the sketch of the apparatus to generate 50,000 ~ 60,000 atm. and 1,400 ~ 1,500°C A , B and C we call belt like apparatus, has a cylinder and two opposed pistons. A was invented by General Electric Company about 30 years ago. This type may be now used at Dubias Company, second largest production. Japanese firm of Tomei Diamond also uses belt like apparatus. Difference among A , B and C is not so much but detailed geometry or shape of apparatus are little different each other. D is dot belt we call modified Bridgeman type apparatus. It has limited inside to utilize but has only two anvils and no cylinder. This type may be now used widely in USSR. E we call cubic anvil apparatus. Cube is compressed from six different directions. This cubic apparatus is now widely used in China. China now produce diamond at different 60 firms. We are developing belt like apparatus in my institute. Unfortunately, this kind of technology is protected by very high secret, so that I'll show you only two or three pictures of industrial production factory. Fig. 9 is Asea Company in Sweden about 20 years ago. Very big press to manufacture diamond is in apparatus. Most important secret may be behind these two persons. But we can see tublar sample assembly, so I can imagine this apparatus may be belt like apparatus. Fig. 10 is also Asea machine, but now may be used by Dubias Company. This mark is combined d and B. Dubias is the largest diamond mine company. They have very big power for natural diamond mining, but also they want to protect even in the industrial synthetic diamond area. Actually they produce almost similar to the General Electric diamond, and this is one picture of the factory. If we analyse the picture, we can estimate that this apparatus may be belt type.

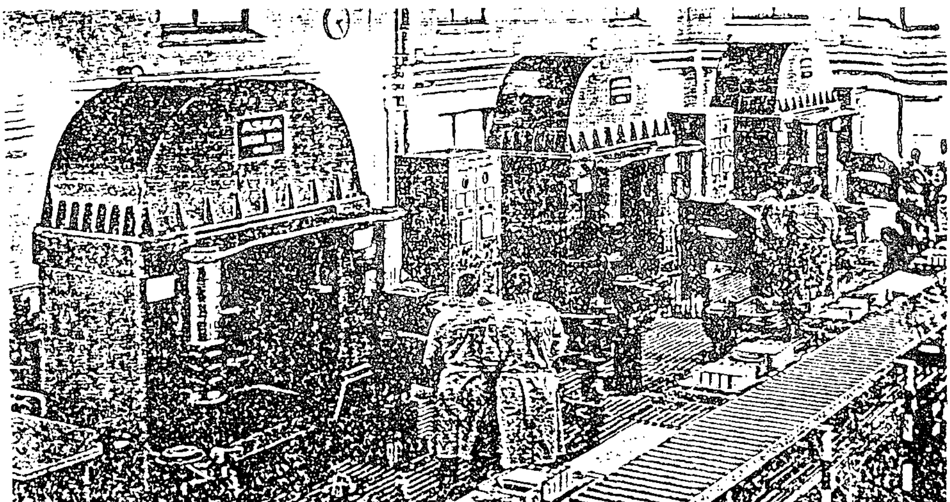


Fig.9

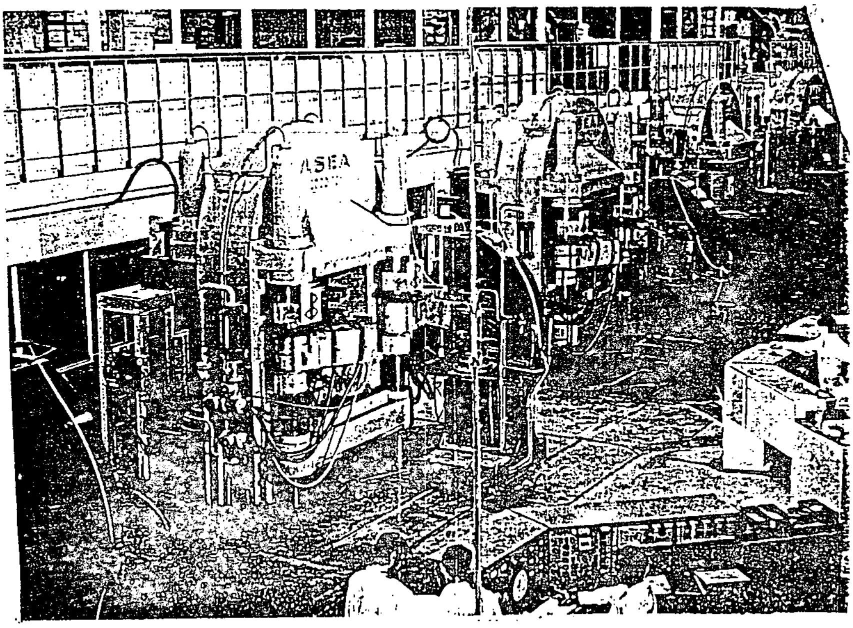



Fig.10 QUINTUS presses for torming of powder material using ultra-high pressure.(F95553)

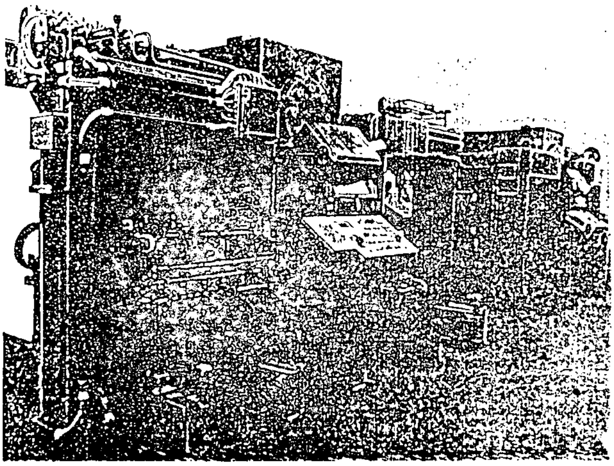


Fig.11

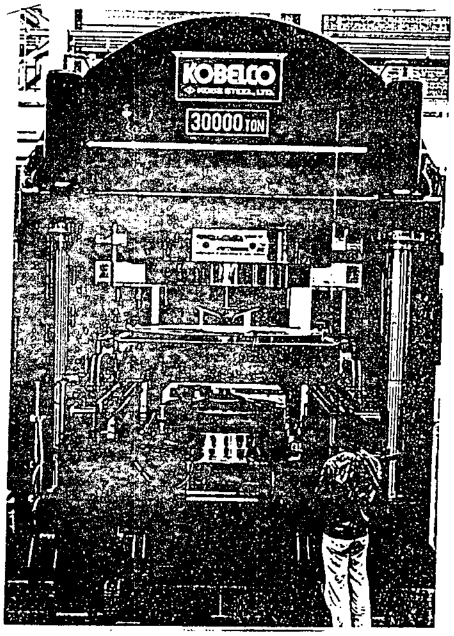



Fig.12 大容量超高速壓力發生裝置
Large Volume Ultra High Pressure Generating Apparatus ( 3萬トンプレス／30,000 ton Press )

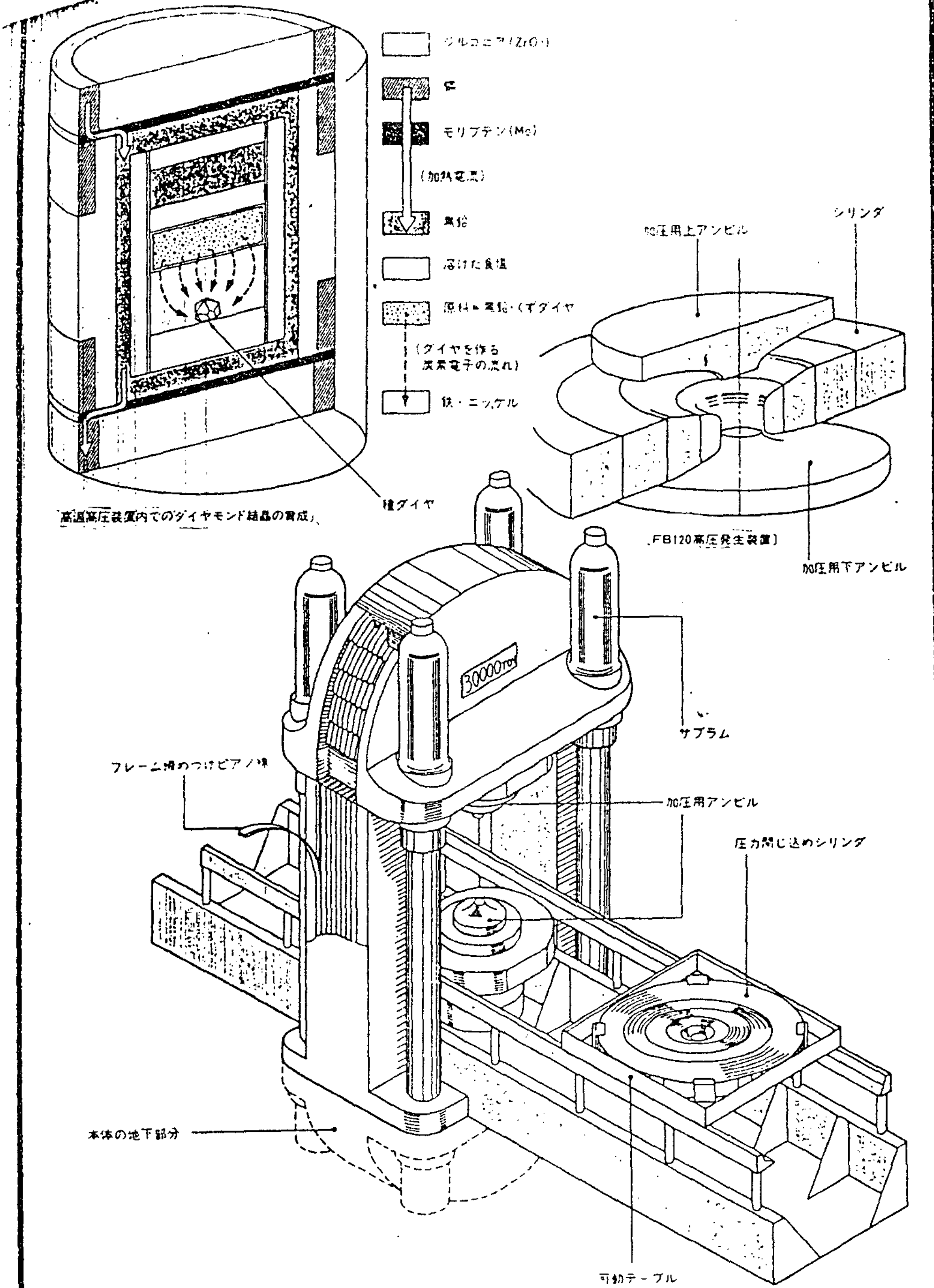



Fig.13　大型超高壓發生裝置 FB 120 の構造

Fig.11 is recently commercialized diamond production or testing machine constructed by one company in West Germany. This is also belt press and at the other part, taking out of the sample from the chamber, setting of sample and turning of sample are carried out. At handling part you can see the hydraulic press. In each hydraulic press at handling station one die now operating, the other die now preparing and comes in, comes out. Fig.12 is our largest high pressure press constructed in 1985. You can see more clearly the belt, anvil and cylinder. The cylinder here is not monoblock and divided by the several binding rings. These rings are set in the press area. Fig. 13 is the furnace part inside the chamber. The furnace is very similar to the furnace for fine ceramics production. Only difference is that we don't want any open area, and

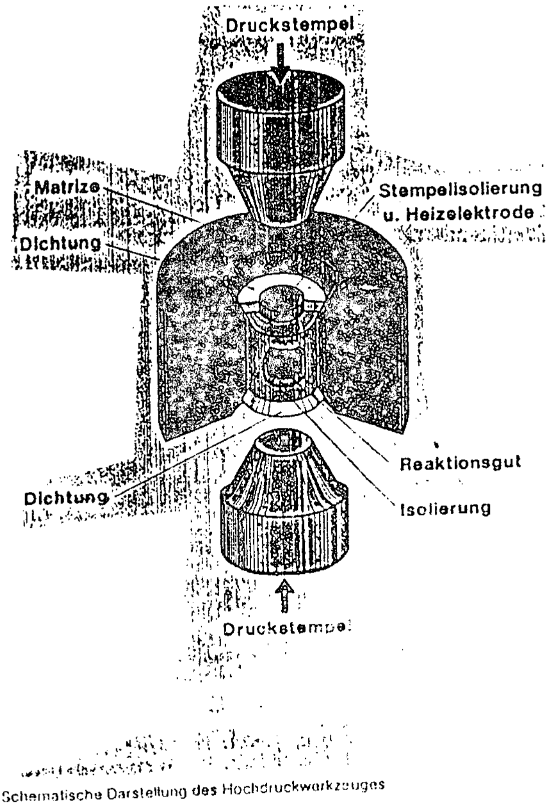



Fig.14

we must pack every kind of things. As packing material we called pressure medium, we normally use NaCl because NaCl is very cheap, very easy to form and has very low shear strength. When we want to produce diamond ceramics, the sample must be sorrounded by hydrostatic pressure field. Gas is the most ideal hydrostatic medium. In the case of NaCl, it does melt at operating condition. So that diamond powder compact are compressed by the molten NaCl. It is like HIP by NaCl medium. In Fig. 14 you can see an apparatus for producing diamond grains. Fig. 12 shows the furnace part and two pistons to push the sample.

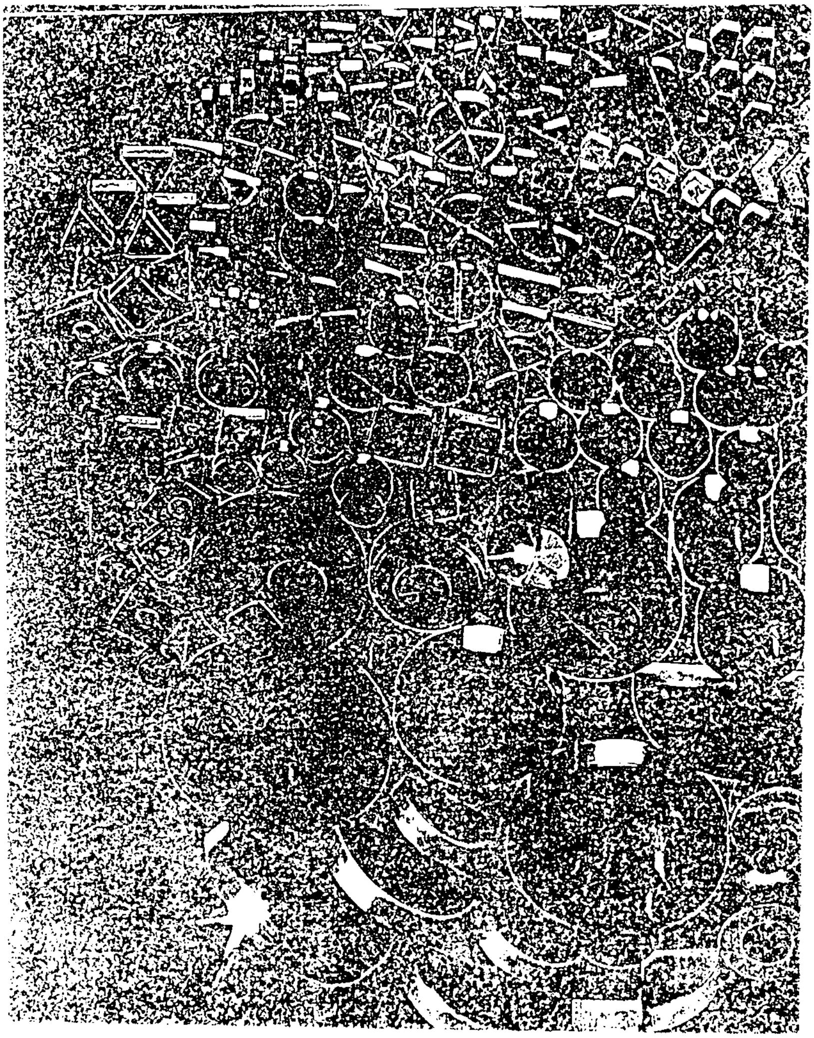


Fig.15

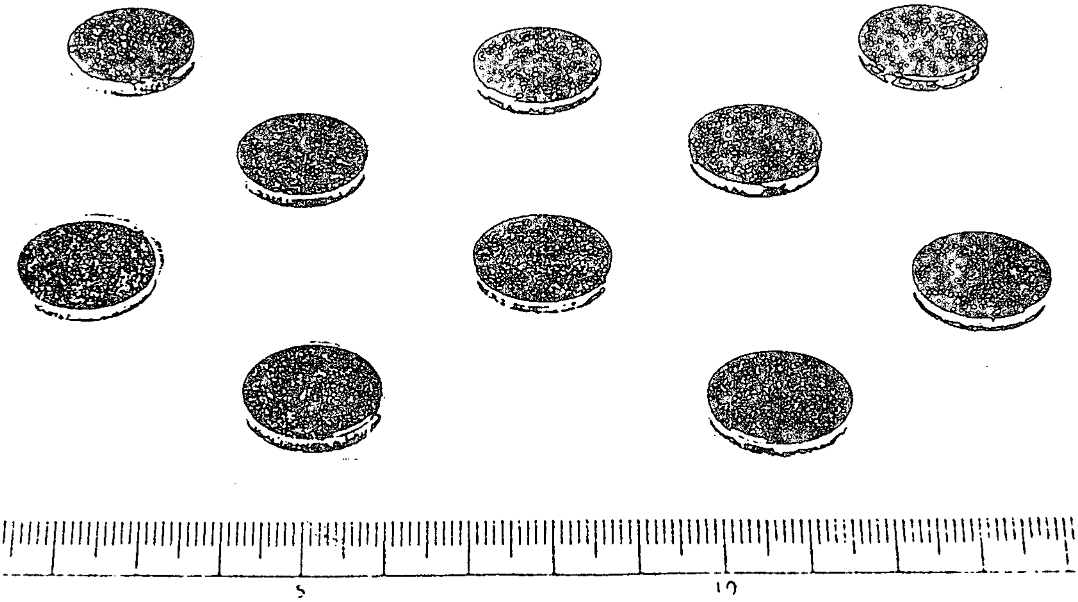
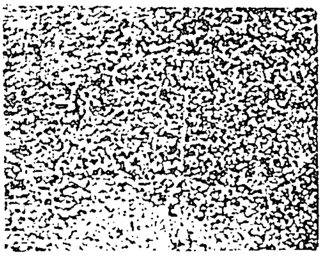
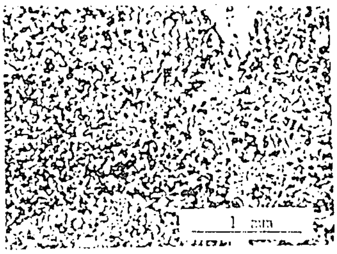


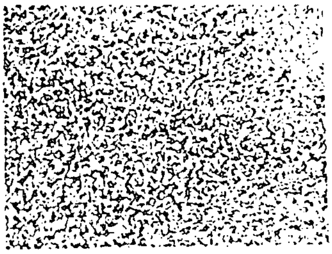
Fig.16 燒結體の大きさ



0 vol % Grophite

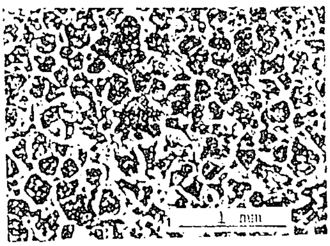



25 vol % Graphite



50 vol % Graphite

75 vol % Graphite




Graphite 100 %

Fig.17

Fig.15 is one example of diamond ceramics commercialized by Dubias Company. You can see very thin diamond ceramics layer, only 0.5mm in thickness, which is binded by WC. Fig.16 is the diamond ceramics we produced. It is similar structure of WC substrate and diamond ceramics layer. Note that the diamond ceramics are not pure diamond. It containe about 10-15% of matalic phase as a sintering agent. The sintering proceeds by liquid phase sintering normally. If we want to modify the diamond ceramics for the purpose of fine ceramic machining, we need more high pure diamond layer. Otherwise, matalic phase is easily expanded and role out the crack source of the fine ceramics in operations. We can control the amount of matalic secondary phase by adding graphite phase to the diamond phase as shown Fig.17. The any graphite in sintering condition can easily converted to the diamond. But if we use 100% graphite, grain size of the ceramics becomes very large and grain boundary layer is almost metalic phase, so that we get diamond ceramics with large amount of secondary phase. If we decrease the amount of graphite and we use only diamond powder. It is not so easy to sinter. We think that between these two condition we can find out the optimum condition to get good sintered ceramics with very small amount of secondary phase.

Fig.18 is the schematic diagram of sintering process of the diamond powder contacted with WC. WC always contains Co as the binding agent. This Co penetrate into the diamond layer. When we use only diamond powder, the amount of penetrated Co is very small. As you see in Fig.14, if we use all graphite powder Co penetrates in large amount. Actually the most optimum condition may exist in some % of the graphite, and this percentage is not so easy to define. But you can imagine that 22 ~ 30% volume % of graphite may be best condition. To get this condition are does not mix diamond and graphite powders because the mixing condition is not so optimum. Instead that we graphitize diamond grains limitedly on the surface area. How to prepare this starting material? It is very easy. If you the diamond powder under the vaccum condition and at about 1,500°C, diamond is partially graphitized because graphite is more stable phase in 1 atm.

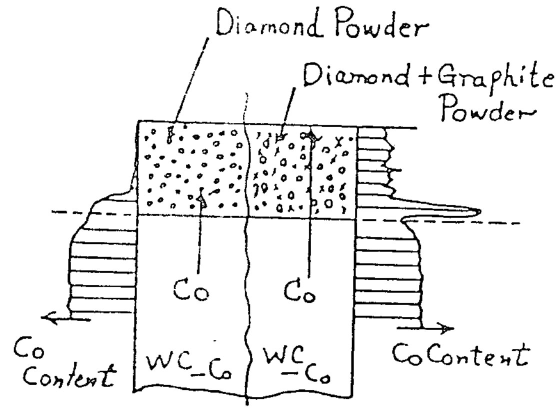



Fig.18

We examined first the cutting tool made by the diamond ceramics we produced by Al-Si alloy. Al-Si alloy is very important for engine part. We increased the amount of Si from 10% to 20%, and cheked how to consume the edge of the cutting tool by observing the length of the waste edge of cutting tool. If we get small value of this Flank wear, it is very highly durable tool.

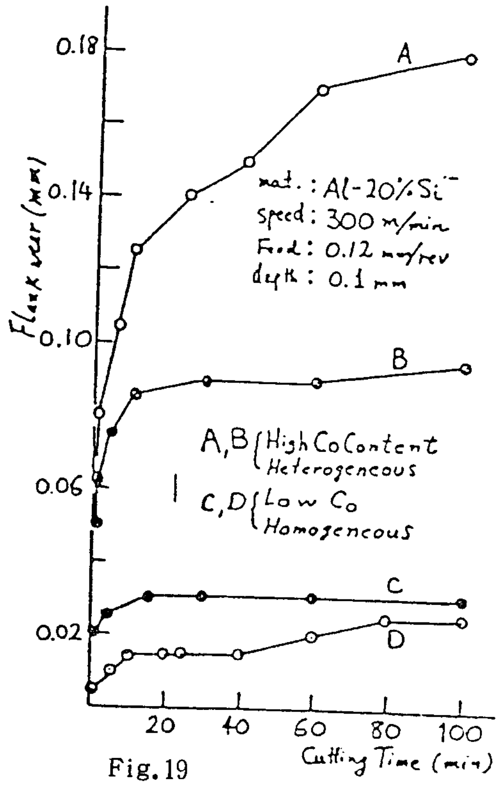



Fig. 19

We tested the tool more than 500 knows and found very small wear. C and D are the case of the diamond ceramics produced using patically graphitized diamond as starting material. A and B are the case, starting powder of graphite and diamond mixtue were used. I'll mention again for Al-Si alloy case in Fig.20. TX and TH are conventional WC tools, these weare very rapidly. Only less than 5 minutes, these wear, 0.1 mm. We cannot use any farther these cutting tools. Natural single crystal stone is very nice, shows very small wearing. But in some cases, it makes cracks and occurs chipping. Compared with conventional tools, the sintered diamond tool shows good results something like that of single crystal natural diamond. Again Fig.21 is high Al-Si alloy case. We changed the amount of the diamond. A is the case of 70% diamond and 30% matalic phase. B is

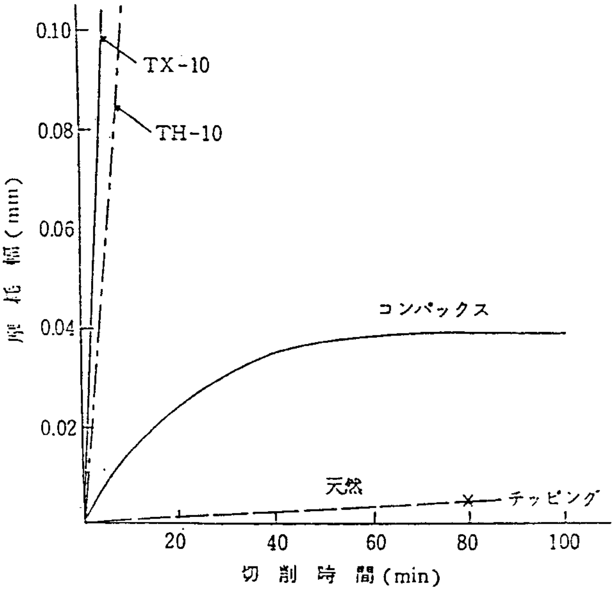



Fig.20 Al-Si 20% T6 合金の切削テスト結果

90% diamond and 10% metalic phase, and grain size is 3$\mu$m. In case of A and B the grain size is relatively small C is 90% diamond, but grain size is 8$\mu$m. In Fig. 18, we can see that as the amount of diamond increases to 90%, 95%, 96.5%, and the grain size becomes large, the wearing become lower. We think these tools can be used for fine ceramics machining. We conventionally must grind fine ceramics, but normally grinding takes about 10 times or more working time. If we grind, for example, 100 minutes, we can cut it in 5 minutes or 10 minutes, more easily and more effectively.

Fig.22 shows again the width of Flank and time of cutting. We tested it by $Si_3N_4$ ceramics, $Al_2O_3$ ceramics and partially stabilized $ZrO_2$ ceramics. This is rather preliminary report but in this moment we can not machine $Si_3N_4$. I believe still that we can modify, we can improve this

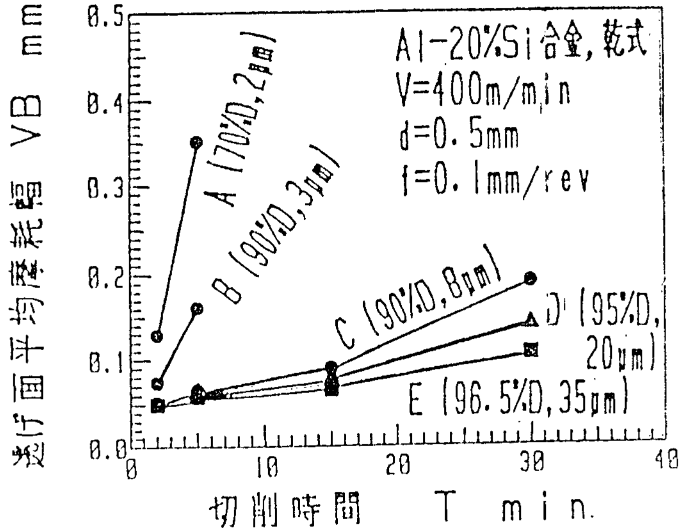



Fig.21 高シリコンアルミニウム合金旋削時の各種ダイヤモンド燒結體工具の時間摩耗線圖

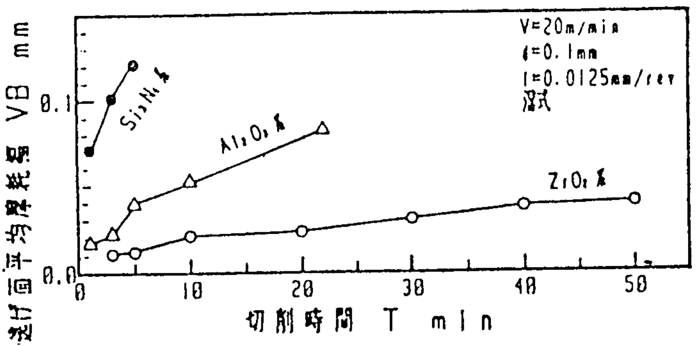



Fig.22 各種 セラミックス旋削時の 時間摩耗線圖

problem, but in this moment we have no more better data. In Fig.22, you see, in $Si_3N_4$ case, only within 3 minutes our wearing exceeds 0.1mm. In case of well sintered $Al_2O_3$, it takes roughly 25 ~ 30 minutes compared with $Si_3N_4$. Although this result is not so fully acceptable and we need more improvement, we can use it as machining tool. But right now we got good data for partially stabilized $ZrO_2$ ceramics. The wear resistance for 50 minutes is still less than 0.1mm. Fig.23 is the surfaces of ceramics after working by cutting tool. You can see very clear shape of running of the cutting tool. Fig. 24 is one example of the machined screw of partially stabilized $ZrO_2$. You see the pitches of 1 mm width.

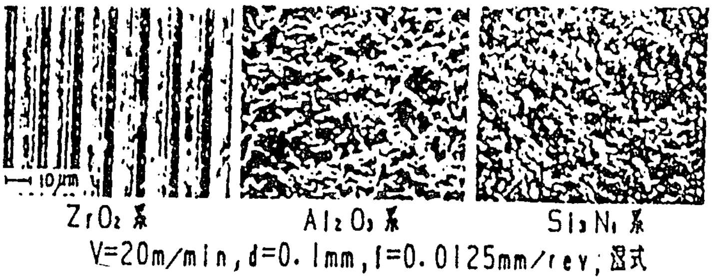



Fig.23　各種セラツクスの加工面性状

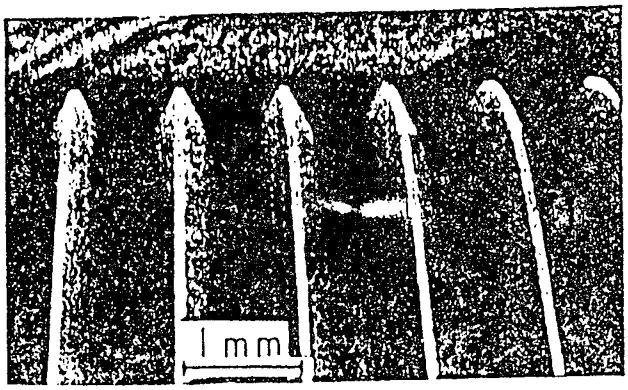



Fig.24　$ZrO_2$ 系セラミツクスのねじ切り

In conclusion, diamond is very difficult to produce, especially diamond ceramic is not so easy to produce in industrial scale, but this kind of ceramics is very hopeful in new future. You must try with wide scope of fine ceramics area, especially machining ceramics area.