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Sintering behaviour of the diamond–cobalt system at high temperature and pressure

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A powder mixture of diamond–8.9 vol % Co was consolidated *in situ* on a WC–10 wt % Co base at temperatures of 1300 to 1500° C under a pressure of 5.8 GPa. The sintered body obtained at 1300° C, which is below the diamond–cobalt eutectic point, was not hard, and the surface of the diamond particle was partially graphitized. On the other hand, the sintered body obtained at 1400 to 1500° C was fairly hard. A strong correlation was also observed between hardness and the cobalt content found in the sintered body. The cobalt content in the harder sintered body was clearly lower compared with that of the softer one. The surface graphitization of the diamond particles is necessary to the transfer of cobalt during the sintering of diamond. In sintering the diamond–cobalt system, the sinterability of diamond was closely related to the feasibility of transformation from diamond to graphite.

1. Introduction

Stromberg and Stephens [1] and Hall [2] have reported the sintering of diamond without additives at high temperature and high pressure. The densities and compressive strength of their resultant compacts reached 3.48 g cm^{-3} and 5.8 GPa, respectively. Hall [2] suggests that transformation from diamond to graphite can be controlled by manipulation of the pressure and temperature. However, the quantitative study of the effect of diamond graphitization on diamond sintering has not been reported. Suzuki *et al.* [3] have also reported the sintering of diamond under similar conditions to those of Stromberg and Stephens [1]. The density and compressive strength of their well-sintered body were 3.2 g cm^{-3} and 4.5 GPa, respectively. They considered that the bonding strength between diamond particles was mainly due to the bonding of the reconverted graphite. They have also investigated quantitatively the degree of graphitization of diamond by X-ray diffraction methods. The degree of graphitization of diamond was more than 25 vol % when treated at 1800° C and 6.4 GPa for 10 min.

Also, Katzman and Libby [4], Wentorf and Rocco [5, 6] and Notsu *et al.* [7] have reported the sintering of diamond in the presence of cobalt. They considered that direct bonding between diamond particles was difficult without the aid of catalyst metals. Katzman and Libby [4] considered the sintering of the diamond–cobalt system as being analogous to the tungsten carbide–cobalt system. Due to a suitable amount of cobalt being necessary to wet the diamond particles, a good sintered body has only been obtained within the narrow range from 16 to 20 vol % Co [4, 7]. However, Wentorf and Rocco [5, 6] used another method in which no binder diamond powder was consolidated *in situ* on the tungsten carbide–cobalt base. They considered that the cobalt in the tungsten carbide layer played an important role as an agent for diamond sintering.

Although the graphitization of diamond has been little studied in the previous works, it is postulated that the graphitization plays an important role for the passing of cobalt melt between the diamond particles, which promotes the sintering.

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2. Experimental procedures

2.1. Sintering procedure

High-pressure sintering was carried out using a modified belt-type high-pressure apparatus with 25 mm bore diameter. The samples were heated by means of an internal graphite heater with 12 mm outside diameter (o.d.), 10 mm internal diameter (i.d.) and 17.4 mm in length. Temperature was measured with a Pt 6 wt % Rh–Pt 30 wt % Rh thermocouple without correction for the pressure effect on the electromotive force. In routine experiments, the temperature was estimated from the relationship between power input and temperature. The pressure was calibrated at room temperature using the known transitions of Bi (2.54 GPa), Tl (3.6 GPa) and Ba (5.5 GPa). Pressure correction at high temperature was made using the melting curve of silver [8] based on the data obtained by piston cylinder apparatus.

The assembly shown in Fig. 1 was used. Fig. 1a is a full illustration and Fig. 1b is an enlarged portion around the sample. Tungsten carbide and diamond powder pellets, as shown in Fig. 1b, were formed into a cylindrical shape under a load of 2 tons. As shown in Fig. 1b, the samples were wrapped with zirconium foil and surrounded by sodium chloride. Sodium chloride has very low shear strength even at room temperature and at high temperature it envelops the sample in an effectively hydrostatic condition.

Recently, Kennedy and Kennedy [9] have determined that the graphite–diamond equilibrium boundary follows the equation

$$P = 19.4 + T/40, \qquad (1)$$

where P is in kbar and T is in °C, which gives an equilibrium temperature of 1544° C at 5.8 GPa. Strong and Tuft [10] have determined that the cobalt–diamond eutectic point is 1336° C at 5.6 GPa. Considering these results, we chose the three conditions of 1300, 1400 and 1500° C at 5.8 GPa for the sintering. The samples were maintained at these conditions for an hour and then cooled to room temperature in about 40 min. As the samples were cooling, the pressure was slowly released in order to minimize the residual strains.

2.2. Starting materials

Commercially available synthetic diamond powder (Komatsu, 0–1 μm and 5–12 μm grade) and cobalt chloride (Wako Pure Chemical Industries, Ltd) were used as the starting materials. Fig. 2 shows scanning electron micrographs (SEM) of the diamond powders. It is very difficult to obtain homogeneous mixing of diamond and cobalt powders. The method used in this study is as follows. The diamond powder was dispersed in $CoCl_2 \cdot 6H_2O$ aqueous solution and then excess water was evaporated while the mixture was being stirred. The powder mixture obtained was reduced in a hydrogen atmosphere at 300° C for one hour and then 600° C for one hour. In a typical experi-

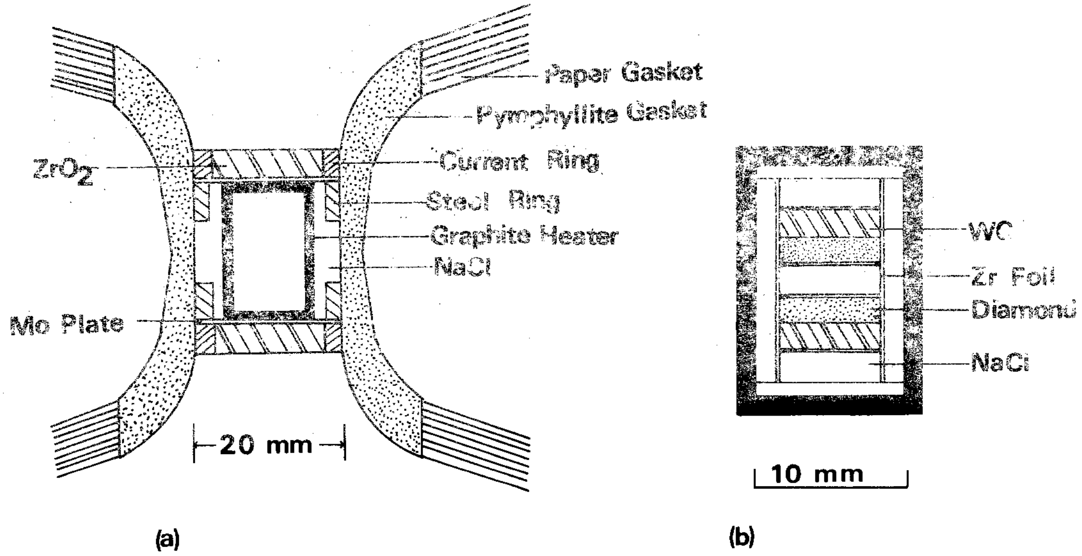

Figure 1 Sample assembly for high-pressure sintering of diamond. (a) Full illustration of the cell; (b) enlarged portion around the sample.

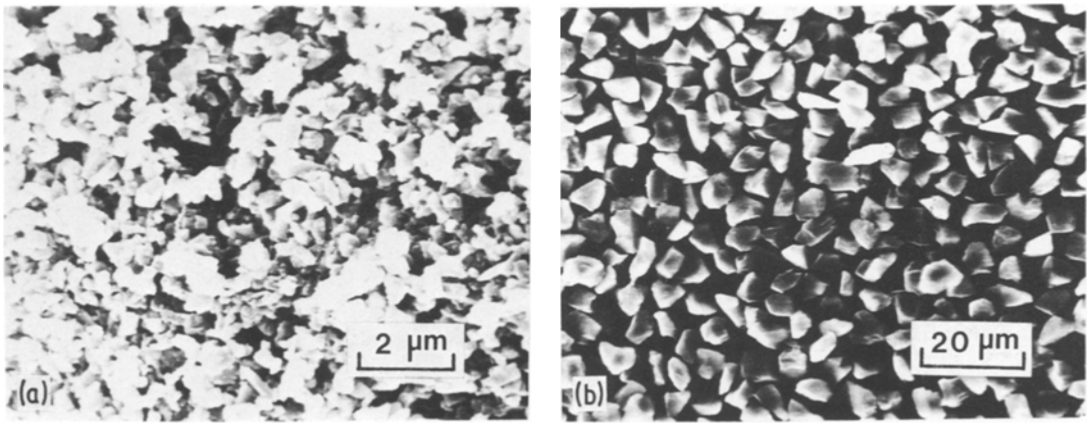

Figure 2 Scanning electron micrograph of the starting diamond powders. (a) 0–1 μm grade diamond produced by static pressure using a metal catalyst. (b) 5–12 μm grade diamond produced by static pressure using a metal catalyst.

ment, the diamond powder was consolidated *in situ* on tungsten carbide–cobalt base. The cobalt contents of the tungsten carbide and diamond layers, which were used in this study, were 10 wt % Co and 8.9 vol % Co, respectively.

2.3. Characterization of the sintered diamond

The samples obtained were characterized by means of electron probe X-ray micro-analysis (EPMA), scanning electron microscopy (SEM), X-ray diffraction, Raman spectroscopy and the micro-Vicker's hardness test. Raman spectra were measured by a Spex RAMALOG 1401 spectrometer, equipped with a third monochromator, using the 514.5 nm line of an argon-ion laser for excitation. The spectra were recorded with a spectral slit width of about 7 cm^{-1}, employing a backscattering geometry. Micro-Vicker's hardness was measured at 100 g load.

3. Results and discussions

When diamond powder (0–1 μm grade) without additives was consolidated *in situ* on tungsten carbide–cobalt powder at high temperature and high pressure, the contact strength between the two layers was relatively weak. In some cases, the sample obtained was separated into diamond and tungsten carbide layers. The contact strength was independent of the cobalt content in the tungsten carbide layer. It was also independent of the source of diamonds in the case of diamonds having the same grain size, but it was dependent on the grain size of diamond. The reason for separation into two layers is not clear, but it is considered to be due to the restriction of the cobalt diffusion from the tungsten carbide layer to the diamond one.

On the other hand, when diamond–8.9 vol % Co powder mixture was consolidated *in situ* on tungsten carbide–10 wt % Co powder mixture at high temperature and high pressure (1300, 1400 and 1500° C at 5.8 GPa), the contact strength between two layers was very high compared with the former experiment. As the sintered diamond composite was covered tightly with Zr foil, the surfaces of the diamond and tungsten carbide were ground with a diamond wheel. On polishing, the samples obtained at 1400 and 1500° C were found to be far more resistant to abrasion than those at 1300° C.

3.1. Relationship between hardness and microstructure

The samples obtained under the three conditions of 1300, 1400 and 1500° C at 5.8 GPa will be referred to as Sample A, B and C, respectively. Cobalt distribution of these sintered products was studied by the characteristic X-ray image of cobalt. Definite changes in cobalt distribution have been observed in Sample B in comparison with that of Sample A. Cobalt distribution in Sample A is shown in Fig. 3a. The distribution is relatively uniform throughout the area of vision. Sample B showed a definite decrease in concentration of cobalt as shown in Fig. 3b. Some cobalt pools are also observed in Fig. 3b and their size is about 5 μm. The cobalt distribution of Sample C shows a similar tendency to that of Sample B.

Micro-hardness of samples with different

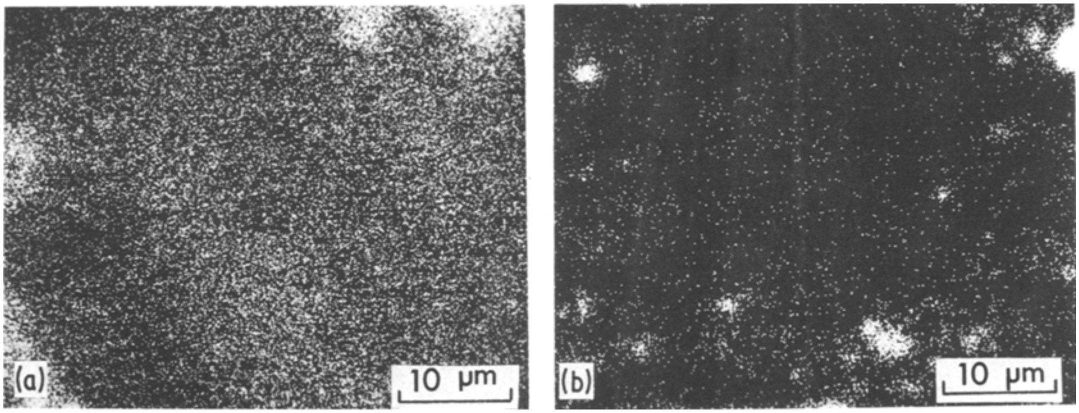

Figure 3 Characteristic X-ray image of cobalt. The lighter area is cobalt and the darker one corresponds to diamond. (a) The image of the sintered body obtained using conditions of 1300° C and 5.8 GPa. (b) The image of the sintered body obtained using conditions of 1400° C and 5.8 GPa.

cobalt distributions was measured on the Vicker's scale. A drastic change in hardness was observed for Sample B, in comparison with that of Sample A. The hardness of Samples A and B had values of 2500 and 7000 kg mm^{-2}, respectively. It was found that the hardness of Sample C was the same as Sample B. The increasing hardness of the sintered product was dependent on cobalt concentration and distribution. The change in hardness and microstructure was also dependent on sintering temperature. The eutectic temperature of Co–diamond at 5.8 GPa was estimated, from the results of Strong and Tuft [10] and Hansen [11], to be higher than 1336° C by a few degrees. In this experiment, the sintering temperature must be above the Co–diamond eutectic point to obtain the fairly hard sintered body.

3.2. Raman spectrum and X-ray diffraction of sintered products

The following results became clear from Raman spectroscopy of the sintered products. The spectra of Samples B and C, obtained by sintering at 1400 and 1500° C, (above the Co–diamond eutectic point at 5.8 GPa), consisted of the Raman line due to diamond. No Raman lines due to graphite were detected. On the other hand, Sample A, obtained by treatment at 1300° C (a temperature below the eutectic point), showed the Raman lines due to highly disordered graphite at 1580 and 1360 cm^{-1}, as shown in Fig. 4, but the Raman line due to diamond was not observed. An X-ray diffraction pattern of Sample A is shown in Fig. 5. It consists predominantly of the diffraction lines of diamond, and the (0 0 2) line of graphite is fairly broad and very weak. This apparent contradiction arises from the fact that each of the diamond particles is covered by a thin layer of carbon. These results show clearly that diamond powders are subjected to surface graphitization in spite of the fact that the sample is kept within the stable region of diamond (1300° C, 5.8 GPa). Diamond powder without additives was treated at 1400° C for an hour under the pressure of 5.8 GPa. The Raman spectra of the samples obtained closely resemble that of Sample A. The reconverted graphite from diamond dissolves into cobalt and then precipitates as diamond under the conditions of 1400 or 1500° C at 5.8 GPa.

3.3. Sintering process of diamond–Co system

The phase diagrams of Ni–carbon at 5.4 GPa and Co–carbon at 5.6 GPa have already been determined by Strong and Hanneman [12] and Strong and Tuft [10], respectively. When both systems are kept in the stable region of diamond, the solubility of carbon is larger than that of diamond at temperature above the eutectic point of the metal–diamond system.

The sintering process of the diamond–Co system will be explained as follows, based on the previous works and the present experimental results. Diamond powders were subjected to surface graphitization under the process of heating and sintering as described above. The reconverted graphite, which is formed on the diamond surface, facilitates rearrangement of diamond particles. The graphite dissolves into the cobalt until the saturated solution is reached and then diamond

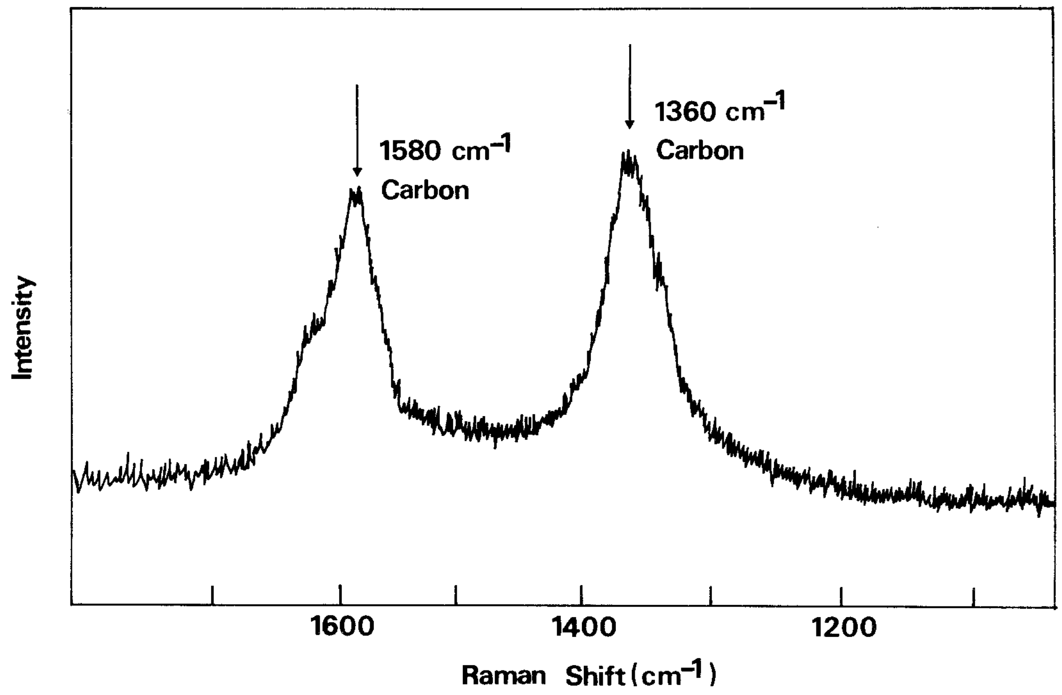

Figure 4 Raman spectrum of the sintered body obtained using conditions of 1300° C and 5.8 GPa.

precipitates from the solution, above the Co–diamond eutectic point. After the precipitation of diamond, the solution can dissolve further graphite and then diamond precipitates from the solution. By the repetition of the dissolution and precipitation process, the cobalt transfers between diamond particles. The transfer of cobalt was clearly noticed in Fig. 3b. On the other hand,

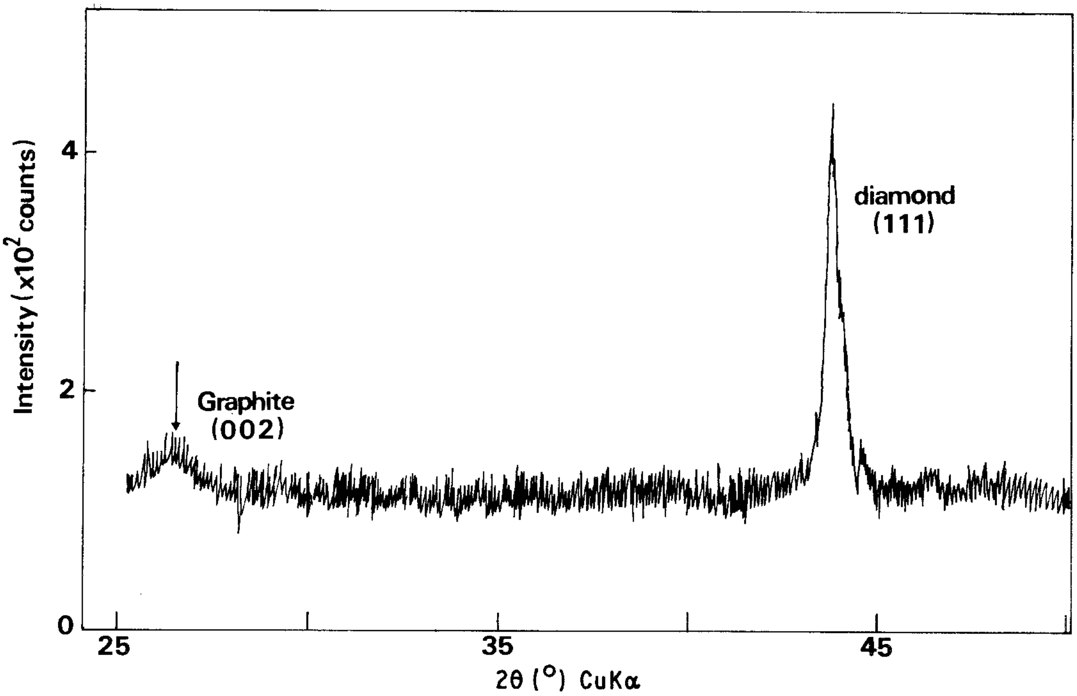

Figure 5 X-ray diffraction pattern of the sintered body obtained using conditions of 1300° C and 5.8 GPa.

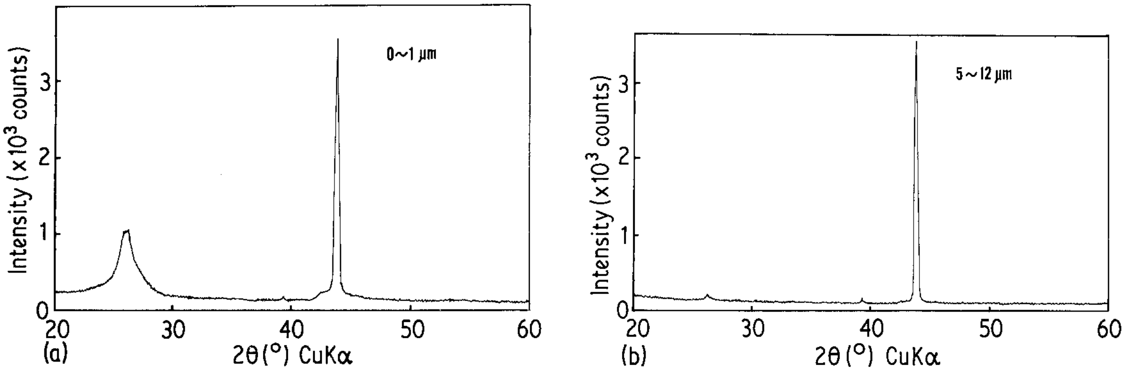

Figure 6 X-ray diffraction pattern of the two types of diamond with different grain sizes after heat treatment at 1400° C and 5 X 10^{-6} torr for one hour. (a) 0–1 μm grade diamond; (b) 5–12 μm grade diamond.

pure diamond cannot dissolve into cobalt beyond the saturated solubility of diamond–Co and then no further diamond precipitates from the solution. The reconverted graphite, which was formed on the diamond surface, plays an important role in the sintering of diamond–Co system.

Sintering, using diamonds with different grain sizes, has been carried out in order to confirm the proposed sintering process of the diamond–Co system. It is assumed that the reconversion behaviour from diamond to graphite will be dependent on grain size and source of diamond. The reconversion behaviour of diamond to graphite was also investigated *in vacuo*. A vacuum of 5 x 10^{-6} torr or better was maintained during heat treatment. Two different sizes of diamond (0–1 and 5–12 μm grade) were treated at 1400° C for an hour in a vacuum. The graphitization behaviour of diamond was strongly dependent on grain size of diamond as shown in Fig. 6. The 5–12 μm diamond powder was extremely difficult to transform from diamond to graphite compared to the 0–1 μm diamond. Two different sizes of diamond were sintered at 1400° C and 5.8 GPa. Drastic changes in micro-hardness have been observed in the sintered body using 5–12 μm diamond in comparison with the micro-hardness formed using 0–1 μm diamond. When coarse (5–12 μm grade) diamond powder was used as the starting material, the hardness of the sintered body was only about 2500 kg mm^{-2}; this is a distinctly lower value than that of the one which was made from fine (0–1 μm grade) powder. As described in another section, the hardness of the product which was produced from the fine powder was above 7000 kg mm^{-2}. The cobalt distribution of these sintered products was also investigated. It was clearly noticed that the cobalt concentration of the fine powder product became less and heterogeneous compared with that of the coarser grained product. The extreme differences in micro-hardness and cobalt distribution between the fine and coarse grained products may be due to the difference of the graphitization behaviour of the diamond.

In the sintering of the diamond–Co system, it is concluded that the presence of sufficient amount of graphite to transfer the cobalt between diamond particles is very important.

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