EFFECT OF RECRYSTALLIZED GRAPHITE ON THE NUCLEATION OF DIAMOND IN FILM GROWTH REACTIONS

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On the basis of experimental phenomena, the dispersion and solution of the carbon source in the solvent-catalyst metal as well as the forming process of recrystallized graphite in the early period of diamond synthesis are analyzed. The effect of the radius of recrystallized graphite formed during synthesis on the diamond nucleation and crystal growth is studied according to the relation of the crystal size and solubility. It points out that, in the diamond stable zone, when the radius of recrystallized graphite is relatively coarse, the solubility will be lower than the diamond crystal nucleus. The coarser and the more recrystallized graphite formed in the preheating process, the smaller the diamond nucleation quantity, and the higher the lower limit of diamond nucleation pressure. During the growth process of the diamond crystal, recrystallized graphite has the effect of adjusting the growing speed of diamond and of providing a carbon source for the crystal in more directions so as to benefit the diamond growth into an integrated single crystal. By controlling the growth of recrystallized graphite during the preheating process, one can control the diamond nucleation quantity to improve the diamond crystal growth conditions.

1. Introduction

Inhibition of diamond nucleation is an important topic in synthetic diamond research. It is well known that the nucleation quantity of diamond can be inhibited by selecting suitable temperature and pressure points in the diamond synthetic zone. Otherwise, it can be definitely inhibited by selecting synthetic carbon material,[1] or adding a nucleation control agent to the solvent-catalyst metal. By analyzing the formation process of the recrystallized graphite during diamond synthesis, we tried to find out the effect of recrystallized graphite on diamond growth, starting off with the solubility of the recrystallized graphite and diamond in the solvent-catalyst metal.

2. Experiment and Conclusions

In our experiment, the samples were prepared under 46 kb and 1400°C; the preheating times were respectively 90 s, 150 s and 240 s. Ball- and branch-shaped recrystallized graphite were found in the three samples preheated for the above times. Under these conditions, the recrystallized graphite in the solvent-catalyst metal has a radius increasing with prolonged preheating time, some have radii up to 25 μm. The result shows that, under given temperature and pressure, the longer the time of preheating, the fewer the number of nucleations.

The samples preheated in the graphite stable zone were metallographically observed by SEM and analyzed by electronic probe. The result shows that there exists in the solvent metal some recrystallized graphite which is found not only in the graphite stable zone but also often in the diamond stable zone, in coexistence with diamond crystal.

3. Discussion

The solvent-catalyst metal used in the diamond synthesis has good infiltration for carbon source graphite and diamond, and the synthetic graphite used as a carbon source is a porous material. When the solvent-catalyst metal is in a state of fusion, the metallic melt erodes the relatively weak part of the carbon interparticle bonding along the open pores of the carbon source and cracks. Some of the grains are dispersed from the carbon source matrix and infiltrate into the cleavage cracks and microcracks in the grains. Some big grains are further dispersed into small ones.

In a dispersion system consisting of carbon and catalytic-solvent metal, in which the structure of

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the catalytic-solvent metal retains short range order under ultra-high pressure and high temperature, it is said that when the (III) plane of the metal can be closed and matched with the carbon atoms on the hexagonal net plane of the graphite microcrystals in the carbon source, the metal atom and the 2 Pz electron of the carbon atom will form a chemical bond like an electrovalent coordinate bond through the empty orbit d of the metal atom so as to weaken the conjugate bond π on the carbon hexagonal net plane and destroy Vanderwall's bond among the stratification planes. The 2 Pz electron of the carbon atom which did not form an electrovalent coordinate bond like in the carbon hexagonal net plane with a metal atom, due to the electron-repelling force from the metal atom, will appear in high probability on the other plane far from the metal atom on the net plane. In the meanwhile, because the conjugate bond π among carbon atoms in the hexagonal net plane is weakened, some folding takes place on the carbon hexagonal ring so as to form the CM structure (C; the carbon hexagonal net plane; M; agglomerates of the melt metal atom corresponding to the atom arrangement on the plane (III) of the face-centered cubic lattice). The formation of the CM structure is a further dispersion and solution of the carbon source, as well as the activation of the carbon atom in a hybridization state of SP^2. The activating extent, which means the extent of the carbon hexagonal ring fold, is related to the pressure. In addition, some of the carbon atoms will be dissolved into the metal melt in an atomic state by means of thermal diffusion, but the carbon dissolved in the melt in a state of nonatomic agglomerate is mainly dissolved into the melt in the form of stable or unstable carbide. When the pressure is relatively low, or the temperature is very high, the carbon dissolved in the metal melt will exist mainly in the form of carbon atoms or carbide. Only when the pressure is relatively high and the temperature is high enough to fuse the solvent metal, but not to destroy the short-range order, can the carbon in the melt exist mainly in the CM structure form.

In the graphite stable zone, when the carbon dissolved in the metal melt exceeds its balance concentration, the atom agglomerates in the CM structure generate recrystallized graphite crystal nuclei by themselves by means of effective collision and deposit and grow on crystal nuclei. During the process of nucleation and growth, carbon atoms on the carbon hexagonal ring net plane will break away from the electrovalent coordinate bond like among metal atoms so as to promote the removal of metal. The carbon atom in the melt and atom agglomerate can also form recrystallized graphite and grow gradually by means of the substrate of stable carbide and the carbon source. As the thermodynamic stability of recrystallized graphite is generally more stable than the stability of the carbon source graphite, the longer the preheating time in the graphite stable zone, the coarser the recrystallized graphite grain, and the more the recrystallized graphite quantity.

In the reaction chamber, there are certain pressure and temperature gradients. The metallic metal has a certain viscosity. The diffusion of carbon atoms, particularly the diffusion of agglomerates of carbon atoms, is limited. What is more, the grain size in the carbon source tablet is not even, and the pores are not uniformly distributed. Thus, the carbon concentration of the melt has a high gradient. An excess of supersaturation is entirely possible in part of the zone. The higher the supersaturation, the more unstable the energy, and the more beneficial to the crystallization of the metastable graphite.[2)] The recrystallized graphite will be found in part of the zone. When the recrystallized graphite is coarse and after it gets into the diamond stable zone, even if it is in a state of solution, it will exist for a certain time.

In the coexistent system of diamond and recrystallized graphite, when the carbon concentration in the metallic melt becomes relatively high, part of the dissolved carbon will crystallize on the recrystallized graphite in order not to make the diamond growing speed too fast. But when the carbon concentration in the metallic melt is relatively low, part of the recrystallized graphite will redissolve so as to make the diamond growth have a sufficient carbon source.

To sum up, both the recrystallized graphite and the carbon source for the diamond growth are carbon atoms dissolved in the solvent-catalyst metal and agglomerates of carbon atoms. The more and the coarser the recrystallized graphite, the fewer the number of diamond nucleations, and the higher the low-limit pressure for diamond nucleation. During the diamond crystal growing process, the recrystallized graphite has the effect of adjusting the diamond growing speed and providing a carbon source for the crystal in more directions so as to benefit the diamond growth into an integrated single crystal. By controlling the growth of recrystallized graphite, one can control the nucleation quantity of diamond in order to improve the growing conditions for diamond crystals.

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