Interface between metallic film from Fe-Ni-C system and HPHT as-grown diamond single crystal ①

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Abstract: Microstructures of surface layer (near diamond) of the metallic film from Fe-Ni-C system are composed of $(Fe, Ni)_3C$, $(Fe, Ni)_{23}C_6$ and γ-(Fe, Ni), from which it can be assumed that graphite isn′t directly catalyzed into diamond through the film and there exists a transition phase $(Fe, Ni)_3C$ that can decompose into diamond structure. AFM morphologies on the film/diamond interface are traces preserved after carbon groups moving from the film to diamond. The morphologies on the as-grown diamond are similar to those on corresponding films, being spherical on (100) face and sawtooth-like steps on (111) face. Diamond growth rates and temperature gradients in boundary layer of the molten film at HPHT result in morphology differences.

Key words: Fe-Ni-C alloy; synthetic diamond; metallic film; interface

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1 INTRODUCTION

Although diamond particles were synthesized successfully at high pressure and high temperature (HPHT) in 1954[1], some issues such as the metallic film surrounding diamond require to be addressed. As we know, there is a molten metallic film surrounding the growing diamond in the course of diamond growth under HPHT, by means of the method that graphite discs are placed alternatively with catalyst discs. As diamond crystal grows toward graphite, this film will isolate the growing diamond from graphite and it will expand like a balloon. However, despite the enlargement of the film, its thickness remains to be less than 100 μm [2] The fact that carbon atoms can diffuse through the film and be catalyzed into the diamond has been reported[2-4]. Much information about diamond growth under HPHT can remain in the film at room temperature because the cell assembly is cooling rapidly after finishing the synthetic process. It is believed that the film/diamond interface can play a very important role in the diamond crystal growth, because the transportation of carbon atoms from the film to the growing diamond is achieved on the interface. Therefore, the investigation of the interface may be one of the attractive ways for explaining the diamond growth mechanism. It is estimated that the reason of few reports on the metallic film so far is the extreme

difficulty of the film sample preparation for observation, because it is very small in size and can be separated hardly from the graphite discs or diamond single crystals.

For explaining the diamond growth mechanism, it is necessary to identify the phase structures of surface layer (near diamond) of the film, using transmission electron microscopy (TEM). Atom force microscopy (AFM) has been proved to be an effective and powerful tool to investigate the morphologies on various as-grown crystals and films to reveal the information of growth mechanism because a variety of morphologies of crystals and films depend on their growth conditions.

2 EXPERIMENTAL

The diamond was synthesized by HPHT method in the presence of Fe-Ni alloy catalyst. As starting materials, the graphite discs (purity 99.9%) were placed alternatively with discs of Fe-Ni alloy. The high-pressure experiment was carried out in a belt-type cubic anvil apparatus. This cell assembly was brought up to a pressure of 5.5 GPa by the high pressure apparatus and then heated to a temperature of approximately 1 300 ℃. After keeping the sample at this temperature for 15 min, the temperature was decreased rapidly by turning off the electric power. Af-

ter this, the cell assembly was taken out from the cubic anvil apparatus and then broken up so as to separate the graphite and the solvent metal discs. The metallic films, which were peeled off carefully from the graphite matrix under the observation by optical microscope, were ground by ion beam milling for TEM observation of their interface structures using Philips CM-30. After that, the films and the diamond particles were respectively placed on the glass flakes gelatinized and then observed using SP13700/300 atom force microscope.

3　RESULTS AND DISCUSSION

3.1　Microstructures of film near diamond

　　Fig. 1 shows a residual plano-concave pit on the cross-section of catalyst (solvent metal)-graphite after peeling off the as-grown diamond, whose shape is homologous with that of diamond, being cube-octahedral. It can be illustrated that the diamond nucleates at the catalyst-graphite boundary (indicated by the arrows in Fig. 1) and grows towards graphite at HPHT; the molten metallic film from the Fe-Ni-C system isolates diamond from graphite disc. Meanwhile, even the surface on the film can be also observed in Fig. 1.
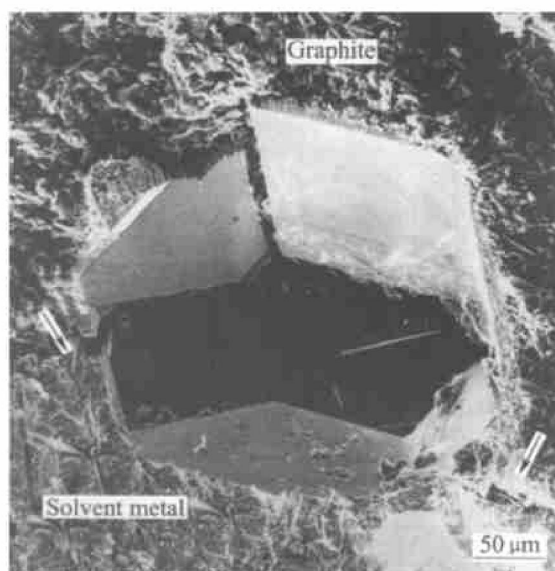

Fig. 1　SEM image of plano-concave pit at boundary between solvent metal and graphite after peeling off diamond

　　TEM analysis method was used for identifying the phase structures of the film near diamond. An interesting phenomenon is that there do not exist graphite and amorphous structures in surface layer about 300 nm in thickness, and there are only (Fe, Ni)$_3$C and (Fe, Ni)$_{23}$C$_6$ particles, as well as γ-(Fe, Ni) stripes in it. Their TEM images and corresponding patterns are shown in Fig. 2 and Fig. 3, from

which their two-dimensions are about several hundreds of nanometers. It has been established
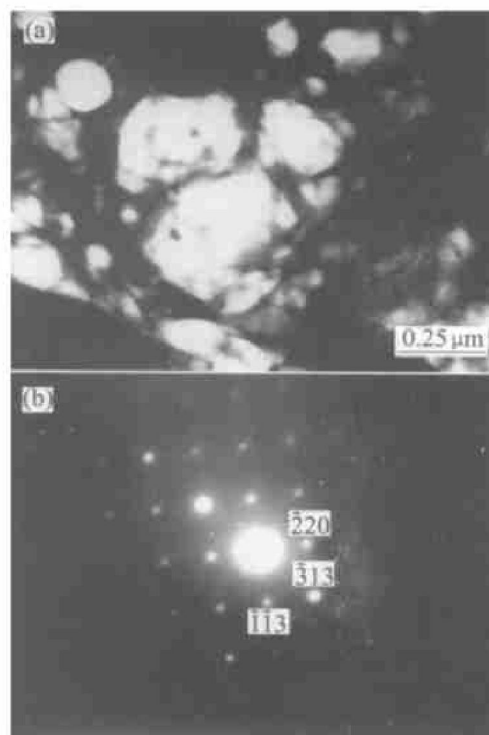

Fig. 2　TEM image of face-centered cubic (Fe, Ni)$_{23}$C$_6$ particles in metallic film(a) and corresponding SAD pattern to (Fe, Ni)$_{23}$C$_6$ from zone axis of [3 2 7] (b)
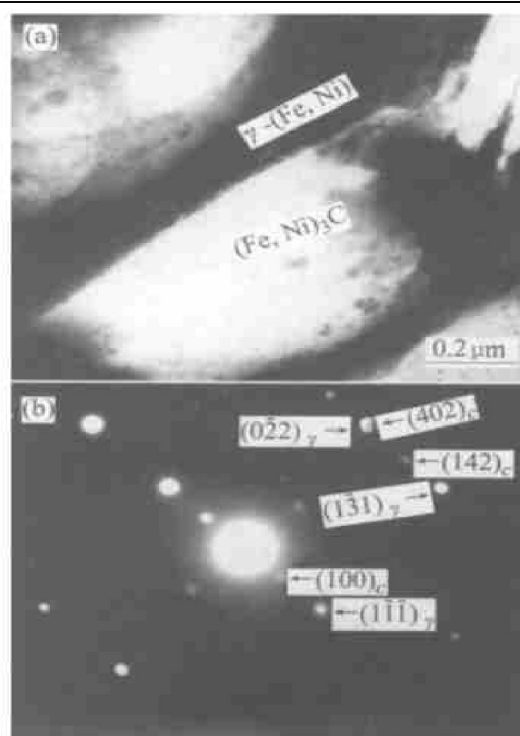

Fig. 3　TEM image of face-centered cubic γ-(Fe, Ni) and orthorhombic (Fe, Ni)$_3$C in metallic film(a) and corresponding SAD pattern from multiple zone axis of γ-(Fe, Ni) [211] and (Fe, Ni)$_3$C [0 1 2] (b)

that the graphite is continuously dissolved in the molten metallic film at HPHT. So the graphite structure can be broken and makes a transition to diamond structure under the effect of the metallic film, but it is not directly catalyzed into diamond structure in the film. Because the only carbon resource for the diamond growth is from graphite disc, it must be certain that there exist(s) transition phase(s) in the metallic film in the course of diamond growth, and the transition phase(s) can be continuously resolved into diamond structure. If there is a nucleated diamond nucleus, the carbon atom groups with diamond structure from the transition phase(s) will separate out from the film and then are continuously stacked on the growing diamond through the film/diamond interface. Of three structures found by TEM, the transition phase might be $(Fe, Ni)_3C$ because it is a carbon-rich phase. Diamond forms usually together with carbon-rich carbides and nickel can promote the decomposition of the carbon iron carbides[5-7]. Phase structures in the molten film under HPHT can remain at atmosphere pressure and room temperature because the cell assembly was cooled rapidly after finishing the synthetic process. So it can be guessed that there exists the carbide $(Fe, Ni)_3C$ that is in short-range order in the molten film at HPHT and it can be continuously resolved into diamond structure. Moreover, the fact that the synthetic temperature of super-quality diamond from the Fe-Ni-C system is within narrow "V" range[8] can also illustrate that there might exist the phases in short-range order for supporting the diamond growth under HTHP. For example, the diamond growth is restricted to the range between the diamond-graphite equilibrium at 1 830 K and the melting of Fe_3C at 1 688 K under the pressure of 5.7 GPa from Fe-C system[9].

3.2 AFM morphology of film/diamond interface

Fig. 4 illustrates an AFM image taken with about $2.5 \times 2.5 \ \mu m^2$ areas, the morphology on the film corresponding to diamond (100) face. The pits are spherical-like and convex, being similar to fine particles on as-grown diamond (100) face[10]. Fig. 5 demonstrates the AFM image conducted in $20 \times 20 \ \mu m^2$ areas on the diamond (111) plane, from which, a well-defined step or terrace structure with homogeneous average step height can be found. The height of the steps could be measured by corresponding section analysis, about 10-20 nm. The AFM image conducted in $5 \times 5 \ \mu m^2$ areas on the film corresponding to diamond (111) plane is shown in Fig. 6. It is clear that the step topography is similar to that of the dia-

mond (111) plane, and the height of steps is about 8-20 nm, which is very close to that on the diamond (111) plane. As for the diamond growth, it is undoubted that the fine particles and interlayer steps on as-grown diamond are from the molten metallic film from Fe-Ni-C system under HTHP, i.e., from transition phase $(Fe, Ni)_3C$ in the film near diamond.
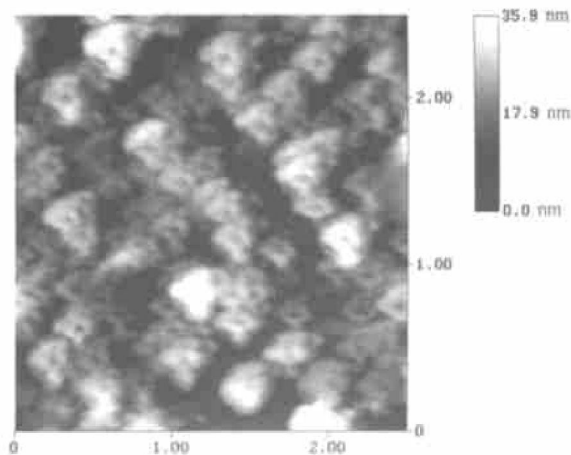

Fig. 4 AFM image ($2.5 \ \mu m \times 2.5 \ \mu m$) on metallic film corresponding to diamond (100) face

Based on the results mentioned above, the morphologies on the film/diamond interface are traces preserved after carbon atom groups are transported to growing diamond. However, the morphology on diamond (111) plane is different from that on (100) plane, which may be the stability difference of film/diamond interface according to the theory of crystal growth in solution[11, 12]. The interface shape is highly sensitive to crystal growth conditions, and can reflect growth process. Superfluous solute atoms can influx in front of the molten film, forming a boundary layer at HPHT, so the increase of solute carbon in the layer will result in supercooling zone called component supercooling. In the course of diamond growth, because of the supercooling zone in the boundary layer, the crystal growth interface would be unstable, which leads to dendritic interface on the crystal[12, 13]. The more positive temperature gradient is in the boundary layer, the more solute carbon dissolves in it, the more easily the narrow supercooling zone forms in front of the interface, the more easily the dendritic interface forms on the growing diamond. At the same time, the positive temperature gradient in the molten film can also be influenced by disturbance under the practical conditions of diamond growth at HPHT, therefore the protruding edges will also be generated. However, these protruding edges cannot develop unlimitably because the solution apart from the interface is in a superheating state, so stable shape can be kept on the interface. The entire disappearance of the surface dendritic patterns on as-grown diamond crystals also makes
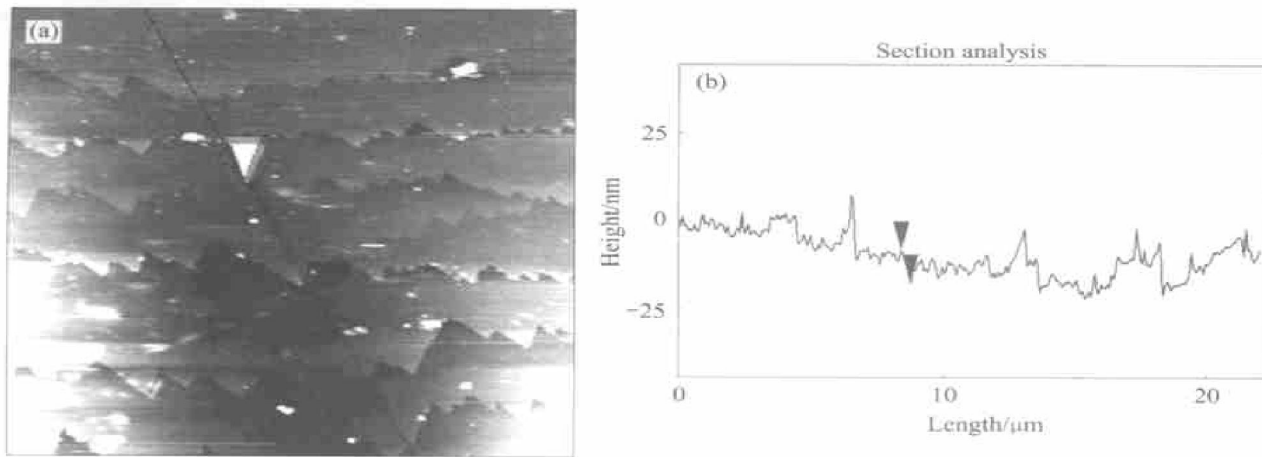
Fig. 5 AFM image (20 μm × 20 μm) of sawtooth-like steps on diamond (111) face(a) and section analysis shows that the height of a step is about 10. 33 nm(b)
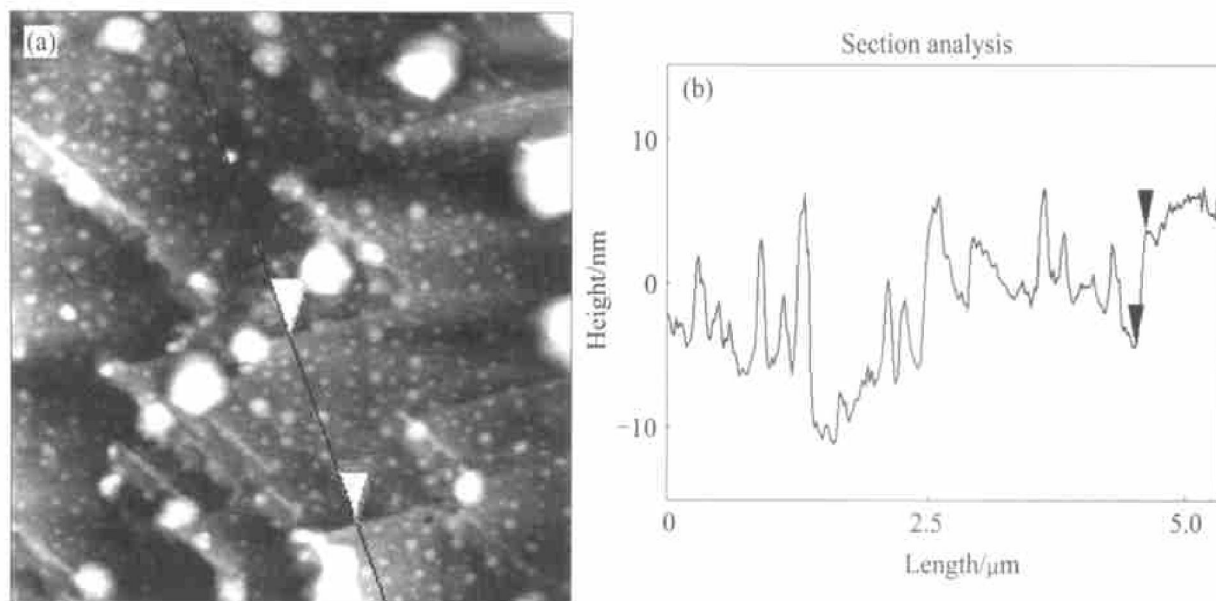

Fig. 6 AFM image (5 μm × 5 μm) on metallic film corresponding to diamond (111) face(a) and section analysis shows that the height of a step is about 8. 89 nm(b)

a contribution to the ubiquitous occurrence of the fine diamond particles and the interlayer steps on as-grown diamond crystals[14], because of the temperature gradients under the synthetic conditions in this paper. Furthermore, the fast growth rate on crystal plane will also bring on rough one. It is generally believed that the growth rates on diamond { 100} are several times higher than that on its { 111}. According to Kanda et al[15], only { 111} faces grow by a layer or spiral growth mechanism, whereas { 100} faces are rough in natural diamonds. The results obtained by AFM in this paper accord with the report by Kanda et al.

4   CONCLUSIONS

1) Microstructures of the surface layer (near dia-

mond) of the molten film from Fe-Ni-C system are composed of (Fe, Ni)$_3$C, (Fe, Ni)$_{23}$ C$_6$ and γ-(Fe, Ni), so the graphite cannot be directly catalyzed into diamond in the molten film at HPHT. There exists transition phase (Fe, Ni)$_3$C in the layer, from which carbon atom groups with diamond structure can be decomposed. The groups are continuously transported to the growing diamond through the film/ diamond interface under diamond growth.

2) The morphologies on the film/ diamond interface were investigated by AFM. It was found that the morphologies on as-grown diamond are similar to those on corresponding metallic film, being spherical on (100) plane and sawtooth-like steps on (111) plane, which are the remaining traces after carbon atom groups moving. The diamond growth rates and temperature gradients in the boundary layer of the molten film at HPHT result in the morphology differ-

ences.

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