Quantitative Evaluation and Enhancement of the Toughness of CVD Diamond Films(気相合成ダイヤモンド薄膜の定量的強度評価と高じん性化)

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論文内容要旨

Chapter 1　Introduction

The unique properties of diamond are yet to be tapped for a large number of advanced materials applications. Fascination with this king of all gemstones has turned into excitement recently with the development of techniques for produce of crystalline diamond films and coatings using low-pressure gases, rather than the high pressures and temperatures previously considered major. These developments will guide to a new era in diamond technology and offer the potential for exploiting the unique properties of diamond in applications ranging from coatings for bearings and cutting tools to freestanding windows and lens coatings for visible and infrared (IR) transmission, and to thin films for high-temperature and high-power semiconductor devices.

At room temperature diamond behaves as an ideal brittle material. Toughness of these CVD diamond films was measured by Drory et al. by using standard fracture toughness specimens (just for the case of films having 400 μm thickness), and reported to be 5.3±1.3MPa·$m^{1/2}$ (15-40J/m^2). Although this amount of toughness is far larger than the weakest cleavage energy of diamond crystal, it is still brittle. Toughness of interface between CVD diamond films and non-diamond substrates was seldom measured, but generally it is expected to be seriously low. In contrast to the excellent physical properties, brittleness of diamond films and their interface could be the most critical disadvantage for many applications to ensure mechanical integrity. As a consequence, the current market of CVD diamond becomes very limited compared to what was expected when CVD technique for diamond was first established.

Diamond films produced by present CVD methods have polycrystalline characters. Considering diamond as a kind of polycrystalline ceramic material, strength of CVD diamond may possibly be enhanced by optimizing the crystalline microstructure. This thesis presents a study of the enhancement of both the toughness and adhesive toughness of CVD diamond films deposited on the substrates, with the aid of evaluation by newly developed techniques. Finally, the effect of the adhesive toughness on a practical performance of diamond coated cutting tools is surveyed.

Chapter 2 Testing Techniques for the Strength of Thin Films

Prior to the trial to enhance the strength of diamond films, it is essential to establish the evaluation methods for measuring the strength, which also happens to be a difficult task in the case of thin films. Therefore both evaluation and enhancement of the strength of CVD diamond films are the key issues for further expansion of application and as well as better mechanical integrity of CVD diamond structures. The newly developed techniques to evaluate the toughness of diamond films and the adhesive toughness are presented in this chapter. The results that are obtained with the newly developed methods will be discussed in the subsequent chapters of this thesis.

Chapter 3 Adhesive Toughness of CVD Diamond Particles

A recently developed technique has been successfully employed to measure the different adhesive toughness of CVD diamond particles grown with various deposition conditions on silicon wafers and on Co-cemented WC substrates subjected to the different pre-treatments and WC grain size.

Microscopic crystalline morphologies of CVD diamond particles deposited on Si substrate with various deposition conditions were examined in detail in connection to their adhesive toughness. Crystalline morphology was quite sensitive to methane concentration in the source gas mixture, which resulted in a complicated trend of adhesive toughness as shown in Fig. 3-1(b). For the case of particles deposited with 0.5 % methane, SiC interlayer could be observed along the interface. This composition was supposed to be quite brittle with the adhesive toughness of approximately 5 J/m^2. On the contrary, particles deposited with higher methane were polycrystalline diamond with weak π-bonding concentrating in grain boundaries. With an adequate distribution of grain size in the diamond particles deposited with 2% methane, the adhesive toughness was improved to be almost 25 J/m^2. This effect was expected to be due to microcracks and/or slips along grain boundaries, which dissipated more energy. Grain size was actually getting smaller with higher methane concentration, and the adhesive toughness of particles with 5 % methane was again quite low as 3 J/m^2 due to too small grains with more π-bond in finer grain boundaries. As a conclusion, CVD diamond is comprehended as a kind of composite materials composed of strong grains of diamond with weak grain boundaries which have rich non-diamond phase of carbon.

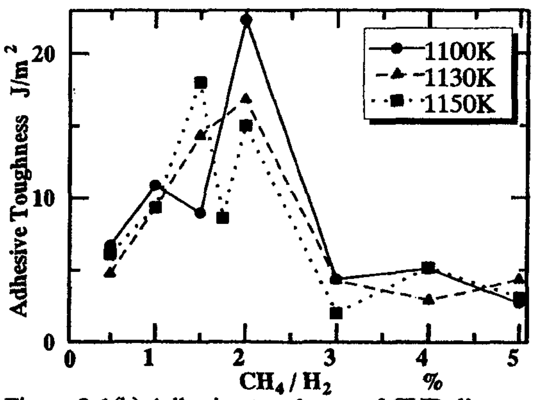

Figure 3-1(b) Adhesive toughness of CVD diamond on Si(100) silicon substrate

On the other hand, the measured adhesion values clearly put into evidence that the WC-Co microstructure also plays an important role on the diamond/substrate interface toughness. In particular, the same pretreatments can give rise to rather different adhesion levels, depending on the WC grain size. Therefore, to achieve a high CVD diamond adhesion, an appropriate combination of substrate microstructure (1 μm grain sizes) and pretreatments (Murakami's etching) should be selected.

These facts suggest that the adhesive toughness of CVD diamond has a potential to be significantly improved by adequately controlling its crystalline morphology and surface pretreatments of the substrate.

Chapter 4 Adhesive Toughness of the CVD Diamond Films and Its Enhancement

The adhesive toughness of CVD diamond films on silicon substrates was obtained by using a recently developed method, which were produced with various methane concentrations in the source gas mixture. The toughness of interface was complicatedly varied with respect to the methane concentration. It was shown that the adhesive toughness of film could be improved by setting an adequate methane concentration. The toughness of interface seems to be in the same trend as the adhesive toughness of diamond particles on silicon substrates with respect to the methane concentration. However, the amount of the adhesive toughness of diamond film was much smaller than that of diamond particle.

Chapter 5 Toughness of the CVD Diamond Films and Its Enhancement

A recently developed technique has been successfully employed to measure the different toughness of CVD diamond films deposited with various methane concentrations on silicon wafers. Figure 5-6 shows the obtained results of toughness.

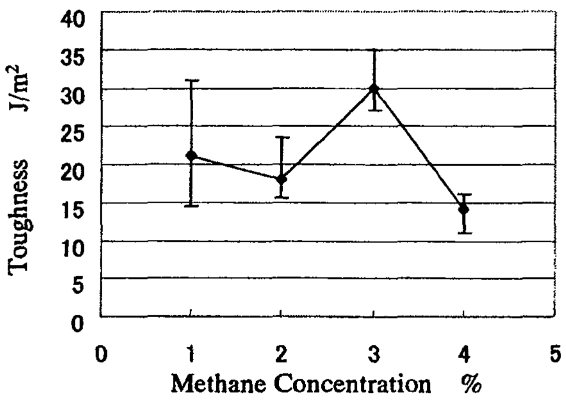

Figure 5-6 Toughness of CVD diamond films

The crack paths which extended in CVD diamond films were observed in detail in connection to their crystalline morphologies. Crystal structures were quite sensitive to methane concentration in the source gas mixture, which resulted in a complicated trend of adhesive toughness. For the case of diamond films deposited with 1.0% methane, diamond film consisted of a lot of small single crystals. This composition induced crack deviations with small angles across the grain boundaries and the toughness appeared to be approximately 21 J/m^2. For the case of diamond films deposited with 3% methane, two different characteristics were observed, which were large single crystals with the (001) smooth facet and the polycrystalline structure composed of smaller crystals. The crack deviations with large angle were observed in both structures. In the polycrystalline structure, a lot of microcracks were observed to be complicatedly twined at the crack tip through TEM observations. As a result of this combination of crystalline morphologies, the toughness was improved to be almost 30 J/m^2. This effect was expected to be due to microcracks, which dissipated more energy. When deposited with 4% methane, the grain size actually became smaller and no smooth facet was observed. The toughness was again low as 14 J/m^2 due to too small grains.

Chapter 6 Effect of the Adhesive Toughness on the Wear Resistant Performance of Diamond Coated Cutting Tools

Endurance of CVD diamond coated cutting tools was surveyed for the first time in quantitative correlation with the adhesive toughness of CVD diamond coatings. Adhesive toughness of diamond coatings strongly depends on the methane concentration in the source gas mixture as mentioned in Chapter 4. The endurance of diamond coated tools was found to follow perfectly the trend of the adhesive toughness with respect to the variation of methane concentration as shown in Fig. 6-5. The endurance of diamond coatings on cutting tools has a clear positive correlation with their adhesive toughness.

Both the toughness and adhesive toughness were examined and enhanced for CVD diamond films in the previous chapters. Their improved toughness leads to the enhancement of real performance of the cutting tools. These results show that the toughness and adhesive toughness are greatly important factors for the practical use of coated tools.

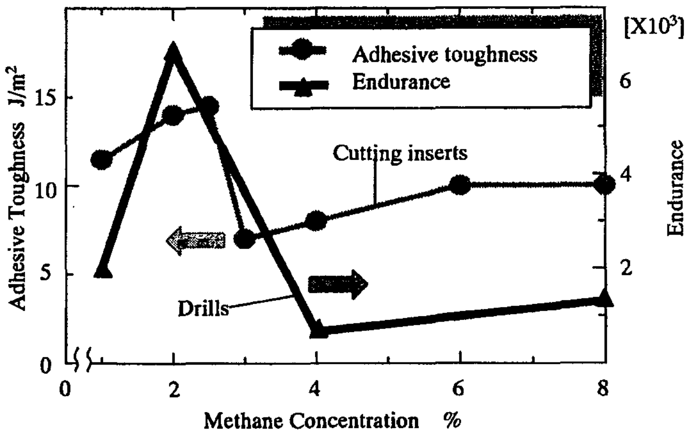

Figure 6-5 Endurance of cutting tools and the adhesive toughness

Chapter 7 Conclusions

As a consequence, the possibility for the enhancement of the toughness of diamond films as well as the adhesive toughness was successfully suggested. In order to find the dominant factors on the enhancement of their toughness, detailed observations were performed on the crystalline morphologies of deposited diamond and discussions were focused on the relationship between their toughness and the crystalline morphologies. It was also clearly shown that enhancement of the toughness leads to the improved reliability of structures which were the diamond coated cutting tools as an example.

This research is the first trial to examine the toughness of CVD diamond films in connection to the crystalline morphologies. The results show that CVD diamond is also a kind of polycrystalline ceramics material and that the crystalline morphologies are quite sensitive to the methane concentration in the source gas mixture. Toughness could be enhanced by setting appropriate deposition condition to optimize the morphologies for higher crack extension resistance, which may further expand the potential of CVD diamond for a wider variety of possible applications by ensuring their mechanical integrity.

論文審査結果の要旨

近年、ダイヤモンドの化学気相合成法が確立され、異種材料基板上のダイヤモンド薄膜の優れた物理的特性を利用する可能性が拓かれた。しかし気相合成ダイヤモンド薄膜は極めて脆弱であり、機械的信頼性の向上が重要な課題となっていた。一方、薄膜材料に関してはその強度評価自体が困難な問題であり、気相合成ダイヤモンドの強度特性の研究は十分とは言い難い状況にあった。

著者は、気相合成ダイヤモンドの強度に関する以上の課題について検討を行い、新しい評価法を開発することをも含めて明確な指針を得ることに成功した。本論文はこれらの考察と検証についてまとめたもので、全編7章からなる。

第1章は序論であり、本研究の背景と目的を述べている。

第2章では、本論文における薄膜の強度評価の指針と、それを具現するために本論文で実際に用いた手法をまとめて説明している。これらの手法は、薄膜そのものの強度と、基板との界面の強度とを独立に、じん性という明確な物理量で評価することに大きな特徴を有している。

第3章では、ダイヤモンドの合成条件、特に原料ガス中のメタン濃度と、基板表面の状態とが界面のじん性に及ぼす影響について、ダイヤモンド粒子を用いた定量評価を行った。強度を向上させる要因について検討した結果、結晶状態により付着強度が大きく変化する事実を見い出した。これは新しい重要な知見である。

第4章では、ダイヤモンド薄膜について界面のじん性の定量評価を行い、粒子の場合と同様、特定の原料ガス中メタン濃度により付着強度が向上することを確認した。これは有益な成果である。

第5章では、ダイヤモンド薄膜そのもののじん性の定量評価を行った。き裂先端を透過電子顕微鏡で直視するという前例のない観察を行い、高いじん性を示すダイヤモンド薄膜には特徴的なき裂進展が見られることを明らかにした。これは重要な知見である。

第6章では、切削工具上の耐摩耗コーティングというダイヤモンド薄膜の具体的応用例を取り上げ、付着強度の向上が工具としての寿命改善に顕著に寄与することを検証するとともに、従来にない優れた耐久性を有するダイヤモンドコーティング工具を作製することに成功した。これは有益な成果である。

第7章は結論である。

以上要するに本論文は、気相合成ダイヤモンド薄膜の新しい強度評価方法を提案し、高強度を得る合成条件を見い出したもので、機械知能工学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。