CVD-Diamond: An Overview of Research and Development at INPE

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Because of its singular properties, wide application, easy to be obtained, and open area for researching, CVD diamond is one of the most important area of investigation in the world. In this work we present the state of the art of our research and development, as an emerging technology for many applications. Emphasis will be given on CVD diamond deposition mechanisms studies when halogenated gases is added to conventional mixtures. Also, investigations of the adherence and stresses between diamond films and several kinds of substrates like cemented carbide, quartz, and Ti6Al4V alloy will be presented. Finally, studies of columnar growth of free-standing films used for developing abrading surfaces including a scaling up for the initial production of a specific CVD diamond device will be presented.

I. Introduction

The first successful attempts to grow diamond at low pressure was contemporary with the High Pressure High Temperature (HPHT) process development[1]. However only around 10 years ago CVD diamond became a reality in the world science and technology[2]. It has a unique set of superior properties and is long recognized to be the material of choice for many applications. Spatial technology area is optimist about the real possibilities of improving the life time of some components by using CVD diamond in spacecrafts as heat sinks, protective coating and tribological devices. At Instituto Nacional de Pesquisas Espaciais-INPE, besides space interest, we are expanding our contribution to some near and long term applications. The scientific community predicted that at the end of the century the number of accumulated papers and patents on CVD diamond will be around five times superior to HPHT diamond, and the industrial production will be around twice superior[3]. The most probable scenario for market depends on the solution of the adherence problem between CVD diamond and several kinds of substrates and the obtainment of large area CVD diamond single crystal, that will open a full market on active electronics. It is postulated that the market in the next century may reach over than hundreds of billions of US dollars. Several works have shown how the theoretical studies are overcoming important stages in order to reach a convincent explanation for the metastable conditions of CVD diamond growth[4-6]. Also, the change of the cost of CVD diamond manufacturing as a function of the different growth techniques and different growth parameters[7] have been accessed. Depending on the application, several acpects as film purity, growth rate, intrinsic and extrinsic stresses, adherence need to be very well understood. In this work, a remark will be given about our studies related to the understanding of growth mechanism using CF_4, CCl_4 and O_2 as additional gases in the conventional mixtures. Optical emission and mass spectrometry measurements were used. In the area of applications most effort was spent to study intrinsic and extrinsic stresses and adherence between diamond film and different kind of substrates. Tungsten carbide, titanium alloy and quartz are mainly considered. Analysis techniques for sample characterization as SEM, AFM, XPS, SIMS, Raman scattering, indentation, were widely used. The variety of devices

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were developed at our laboratory, and one of them will better be presented, including a scaling up evaluation for industrial production.

II. Basic studies

The basic studies at our group is a goal to contribute to find a better explanation about the growth mechanism in metastable conditions. The studies using CF_4 addition in the conventional mixture made possible the improvement of purity and growth rate. The diamond structure was visualized for the first time using atomic force microscopy analysis[8]. The most intense action is to study the species in reaction zone near the substrate surface. Actionometry and mass spectrometry experiments have been strongly used for "in situ" measurements. Optical emission spectroscopy has shown that the relative intensity of H_α (line increases more than 80% for both mixtures H_2/Ar and $H_2/Ar/CH_4$ when the CF_4 concentrations are in the range of 0 to 5%. Similar experiments were made with CCl_2F_2 addition in a H_2/Ar mixtures[9], as shown in Fig. 1a,b.

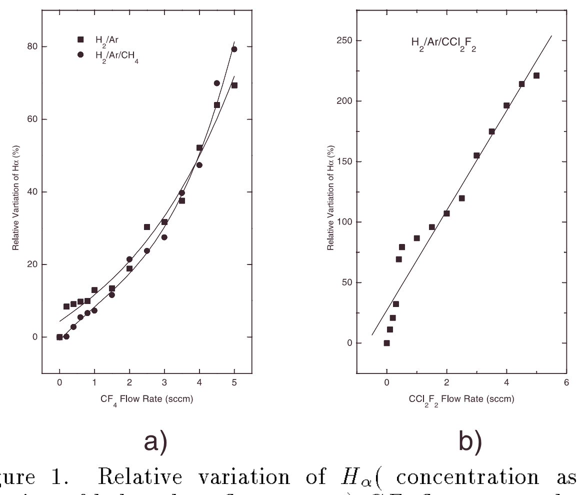

Figure 1. Relative variation of H_α(concentration as a function of halocarbon flow rate, a) CF_4 flow rate and, b) CCl_2F_2 flow rate.

Mass spectrometry was used to analyze the stable species in the exhaust gas. The objective was to observe the differences on chemical paths in the reactor for the two mixtures tested. The analysis showed the increase of C_2H_2 and CH_4 concentration for both mixtures, indicating a fast CF_4 and CCl_2F_2 dissociation mechanism with a fast conversion into the hydrocarbons. For CCl_2F_2 mixture occur HF and HCl formation and the increase of HCl concentration was very pronounced compared with HF increase due to the production of SiF_4. This effect revealed the attack of the quartz bell jar by HF and its possible influence on the whole chemistry in the reactor that is more apparent for CF_4 addition.

These results encouraged us to study better the behavior of activation energy. Measurements of the activation energy constitute an important hole of our contribution to explain how works the diamond growth mechanism. Carefull data compilation from the literature and conveniently normalization of the activation energy show that there is an interesting correlation among them, independently of the growth method and the gas mixture including our results when halogen gases are used. These results are shown in Fig. 2. This may introduce a controversy and so may represent a new open area to be better explored.

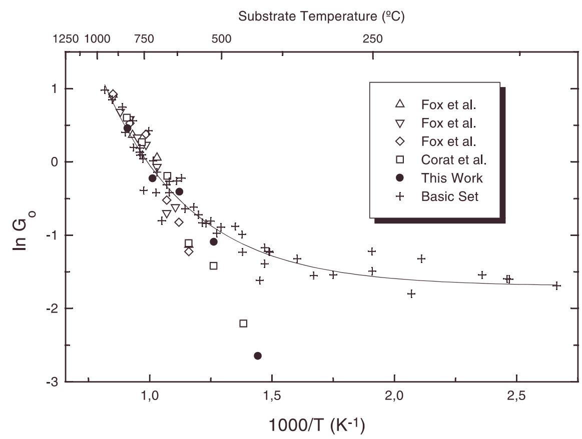

Figure 2. Arrenius Plot showing the activation energy data correlation.

III. Application studies

The ability to deposit thin diamond coatings on several substrate materials and, also, the growth of free-standing diamond pieces in different size and shape opened a wide panorama of applications, including the area of superhard tools. In this section it is presented a brief review of our technology of CVD diamond, with focus on diamond deposition on $WC-Co$, $Ti6Al4V$ and quartz. This section is divided in three parts. The first one provide some results about sample preparation techniques for diamond. Secondly, the problem of film adherence on $WC-Co$, $Ti6Al4V$, and quartz is summarized. Finally, free-standing diamond tools are presented with particular attention to the CVD diamond burrs for dentistry applications. also is presented a scale up for industrial production.

III.1. Surface preparation techniques

There are a lot of techniques of surface preparation for diamond nucleation enhancement. Scratching surfaces with diamond paste or other hard material can increase nucleation density from 10^4 to 10^8 particles/cm^2. Other methods have been developed using a special treatment of the substrate in an ultrasonic bath with diamond powder dispersed in a organic solvent. For this technique a nucleation density up to 10^{10} particles/cm^2 was obtained[10]. However, the dependence of the nucleation density with different preparation technique is not apparently understood. Speculation about the appropriate sits or the presence of diamond dust impinged on surface have been pointed as satisfactory explanation for diamond onset nucleation. Our first investigation, shows a strong dependence of the grain size of the diamond powder in suspension in ultrasonic bath treatment, using hexane as a solvent. Nucleation density around 10^{11} particles/cm^2 was reached on silicon and quartz substrate and no evidence of diamond dust or diamond sit on substrate was found[11]. However, interesting investigations considering the effects of diamond seeding on substrate surface with different dispersive liquids and procedure have also been carried out at our laboratory[12]. This procedure involves mainly two steeps: seeding with diamond powder and a consolidation of the diamond seeds at the substrate surface. From this investigation it became clear how different solvents influence the on set diamond nucleation. Dispersion liquids properties like surface tension, viscosity, vapor pressure, dipole moment and density have been related to nucleation density. Also diamond growth experiments show that exist complete chemical consolidation of the seeded diamond particles onto substrate at nucleation rate around 10^{10} particles/cm^2.

III.2. Adherence studies
CVD diamond deposition on WC-CO substrates

$WC-Co$ cemented carbide is the most studied substrate fo tooling application. Despite being considered the ideal substrate due to its high toughness and relatively low cost $WC-Co$ presents some difficulties for diamond deposition. The presence of cobalt is deleterious to CVD diamond deposition. A large effort in the world have been spent on overcoming this problem. In recent developments we have been able to produce better CVD diamond-coated tool inserts. There are two major obstacles in achieving good adherence between CVD diamond deposit and the $WC-Co$ substrate. One is the mismatch of thermal expansion coefficients ($4.6 \times 10^{-6}/°C$ for WC and $1.1 \times 10^{-6}/°C$ for diamond) which causes large thermal stresses at the interface. The other is chemical interaction between carbon and cobalt that avoids a sufficiently strong bonding between diamond and the carbide. The cobalt content varies from 3 to 12 vol.%. The higher the cobalt content the worst is the film quality. Without a surface preparation step the adhesion strength is very low and the film peels off spontaneously. This occur because the nucleation appears from graphite instead of tungsten carbide. These subjects have been strongly studied [13], so that different techniques of surface preparation definitively contributed to improve the adhesion between diamond and substrate. Our technique of substrate preparation consist of a combination of a chemical etching of the cobalt in ultrasonic bath at controlled deep and a complex compound formation including cobalt and carbon atoms near the surface. The compound formation is reached using a special technique of preparation. Indentation tests have been performed in order to evaluate the adhesion between the diamond film and the substrate. Fig. 3 shows a pour and good adherence from indentation test using a 60 kgf load in a Rockwell C tester. Pour adherence is characterized by big crater because the diamond film peels off from the surface near the indentation region as shown in Fig. 3a. Good adherence is shown in Fig. 3b.

With this results we believe that the process to get good adhesion between diamond film and $WC-Co$ inserts is developed and understood and, and it is for field test in order to figure out the final procedure to get the desired reliability. On quartz surface, similar preparation technique, has been employed and very thin film with good adherence and good optical transmission from UV to IR was obtained[14].

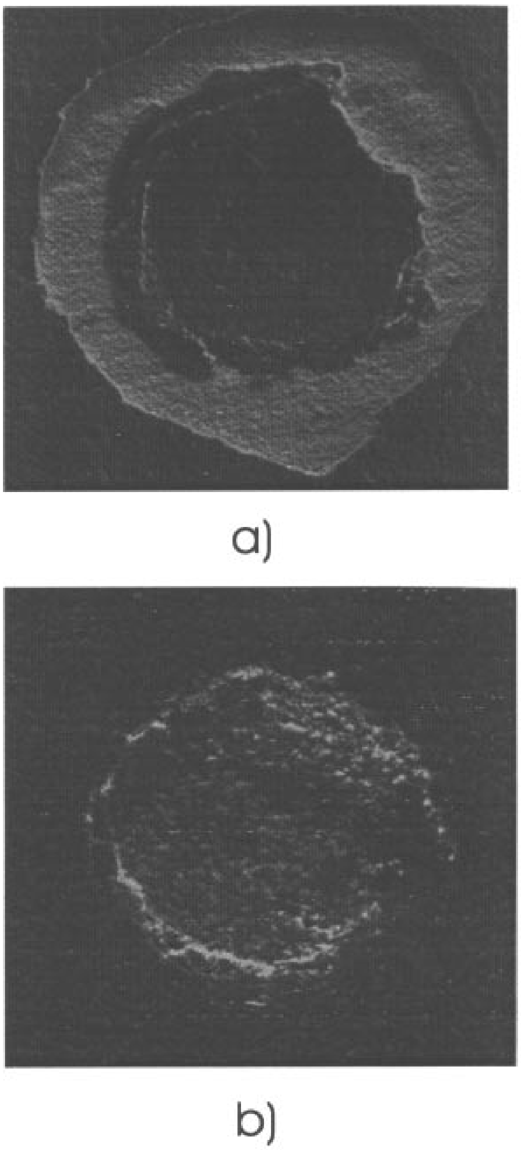

Figure 3. Indentation test on diamond film deposited on $WC-Co$ substrate: a) pour adhesion, and b) very good adhesion.

CVD diamond deposition on $Ti6Al4V$

The extensive use of titanium and its alloys is based primarily on two very important characteristics: high strength-to-weight ratio and excellent corrosion resistance. Including its excellent bio-compatibility, it has been used as prosthesis of multiple uses. Because of its very low wear resistance, the addition of a thin CVD diamond film can give an extended life for many applications. However, the adhesion problems of the diamond film on $Ti6Al4V$ surface is an opened area and requires a deep study. These studies are related to the influence of the thermal coefficient mismatch, structural defects, impurities, and variation of the alloy surface composition during diamond deposition. Nucleation rate and growth parameters were studied as a function of substrate preparation techniques. The best condition of diamond growth on $Ti6Al4V$ was set as a main feature for stress and adherence studies. Preliminary studies have shown that up to 5 μm diamond thin film adhered to $Ti6Al4V$ substrate after growth with heating treatment at the growth temperature. The better conditions for stress relief was also obtained. Hardness testing has shown the substrate recovery as a function of the heating or dehydrogenation time[15]. The original Ti6Al4V structure is partially recovered. It is speculated that the dehydrogenation procedure can be responsible for the adherence enhancement.

III.3. Free-standing CVD-diamond film

Free-standing CVD diamond film represent an important part of already available applications. At INPE free-standing film of thickness from a few microns to hundreds of microns have been obtained. Also processing via laser radiation was completely developed. Different forms of thick free-standing film have been studied using a hot filament assisted technique. For instance, a device for odontological and related uses was completely studied and developed based on columnar growth theory[16]. Even though the production cost of the CVD diamond burr is much higher than the conventional ones, its performance is much superior and the prices need to be evaluated by a cost/benefit ratio. The CVD diamond burrs clearly shows a large advantage[17]. Scaling-up calculations based on standard parameters considerations show a final cost for each piece as a function of the free-standing diamond tip thickness and of the number of reactors working at the same time as shown in Fig. 4. These results show that the cost per piece decreases more with the increase of the diamond film thickness. For 450 μm thick free-standing diamond tips the final cost of each piece may reach a value lower than 1 dollar.

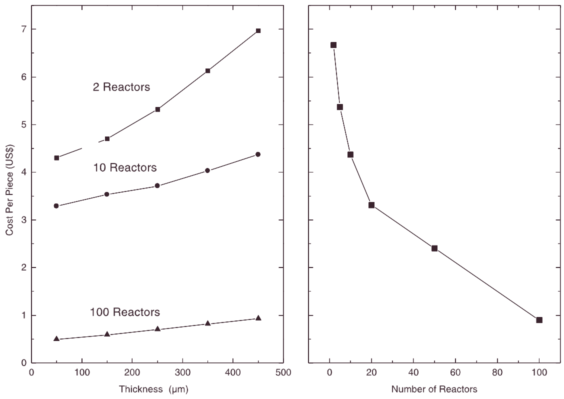

Figure 4. Projected production cost of each CVD diamond burr tip as a function of: a) the film thickness, and b) the number of reactors, for a 450 μm thick film.

IV. Conclusion

We at INPE have been studying thin and free standing CVD diamond films with good up to date results in terms of basic studies and development of applications. Good national and international cooperation have been very helpfull in keeping this development.

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