Pretreatment and Post-treatment for Enhanced Adherence of the Diamond-CVD Films on Ti6Al4V Substrate Using Hot Filament Assisted Technique

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Abstract

High density diamond nucleation and diamond growth on Ti6Al4V substrate has been studied as a pretreatment procedure. An enhanced nucleation was observed using 0.25μm diamond powder suspension in n-hexane in a ultrasonic bath. Continuous CVD diamond films form after 30 minutes growth. Films grown up to 2 hours have also been studied. A post-treatment was also performed to recuperate substrate properties. After growth the substrate was kept in vacuum at the growth temperature for a dehydrogenation procedure. Films as thick as 5 μm remains on the substrate after such procedure, showing a clear improvement of the adherence. Characterizations via Raman Spectroscopy, SEM and EDX are presented.

Introduction

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. Titanium's strength-to-weight ratio has made it a basic structural material for aircraft, aerospace and automotive applications [1]. Its excellent corrosion resistance has already made it attractive for the chemical processing industry, which uses titanium equipment to process acids, organics, caustics and salt solutions [2,3,4]. Also, due to its biocompatibility, it has been used as prosthesis of multiple uses.

Titanium is the fourth most abundant engineering metal in the earth's crust, exceeded only by aluminum, iron, and magnesium. It can be found in rocks, minerals, clays, sands and in the sea. The two most common ores are rutile and ilmenite. The largest commercial source of rutile is beach sand. Ilmenite is found in both sand and rock deposits [5,6].

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 require a deep study. These studies are related to the influence of the thermal coefficient mismatching, structural defects, impurities, and variation of the alloy surface composition during diamond deposition. Relative success have been obtained only for diamond film thickness as low as 1.0 μm [7]. It is an exciting and opened area to investigate.

We investigated the adherence of diamond in other substrate materials. The most important results were obtained on WC-Co for tooling applications [8, 9]. In this case, the preparation of the substrate surface and its modifications have represented the main parameters for successful results. Diamond film as thick as 40 μm was obtained and supported up 60 kgf indentation tests with a Braille tip.

To achieve good adherence between CVD diamond film and the Ti6Al4V substrate, the most important obstacles to overcome are: the mismatch of thermal expansion coefficients ($1.1 \times 10^{-6}/^{o}C$ for diamond and $8.5 \times 10^{-6}/^{o}C$ for Ti6Al4V substrate), which causes large thermal stresses at the interface, and the hydrogen diffusion in sample during growth. Also, the presence of the hydrogen in the bulk of the substrate material has been investigated [10, 11, 12]. This work presents a study of diamond growth on Ti6Al4V substrate, with special attention to the film stress. 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. Also, after this procedure, the sample temperature was reduced at a constant rate, for long periods, up to 4 hours, in order to get the better conditions for stress relief. Hardness testing has shown the substrate recovery as a function of the heating or dehydrogenation time. The original Ti6Al4V structure is partially recovered. It is speculated that the dehydrogenation procedure can be responsible for the adherence enhancement. SEM and Raman Spectroscopy have shown the quality of the film. Semi-quantitative analysis of the titanium, aluminum and vanadium content near the surface was studied with EDX.

Experimental Procedure

Figure 1 shows the experimental setup for CVD diamond growth. It consists of a conventional hot filament reactor with the substrate holder connected to a power supply used for the post-heating treatment of the sample. Diamond deposition was carried out with conventional mixtures of 1.5 vol.% CH_4 in H_2. The total gas flow rate was fixed at 100 sccm and the pressure inside the reactor was maintained at 50 torr. The substrate temperature was measured by a thermocouple and it was kept around 800 C. A 30 minutes

deposition time was used for nucleation analysis. Thick films were grown for 2 hours. All samples (8 mm diameter and 2 mm thickness) were machined from the same Ti6Al4V rod. The Ti6Al4V substrate surface was treated using diamond powder of 0.25 μm grit in *n*-hexane ultrasonic bath (1g/20ml) during 5 minutes. This procedure has been identified as the best condition for high nucleation density [13], including for Ti6Al4V substrate.
A post-growth heating procedure was carried out keeping the substrate at growth temperature (800-820 C) in gross vacuum condition for a determined time, after diamond growth. The objective of this procedure was to promote Ti6Al4V dehydrogenation.

Results and Discussion

First of all, the nucleation enhanced has been studied. The good quality film and high nucleation density reached helped to improve the film adhesion, but it was not sufficient to avoid the film peeling from the substrate after the growth. The morphology uniformity, the grain size and the thickness of the as grown diamond films were estimated by scanning electron microscopy (SEM). The SEM micrograph of the 0.25μm diamond powder seeded substrate is shown in figure 2a. The substrate is covered by a small and uniform layer of diamond particles. Figure 2b shows a good sharpness and uniform grains after 30 minutes in growth conditions.

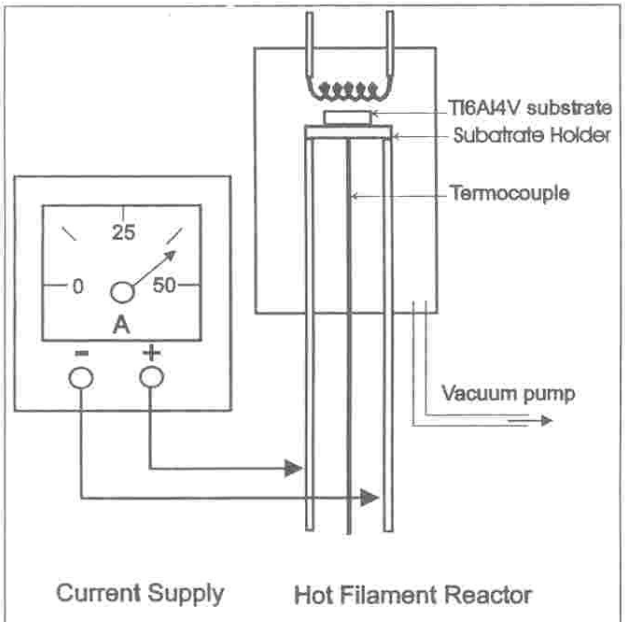

Fig. 1 - Experimental setup showing a hot filament reactor and the current supply for post-heating treatment.

The presence of the hydrogen in the bulk of the substrate material has been investigated. Indentation testing on Ti6Al4V showed different substrate hardness before and after diamond growth. We observed 47 Rockwell-A before diamond growth and 72 Rockwell-A after diamond growth.

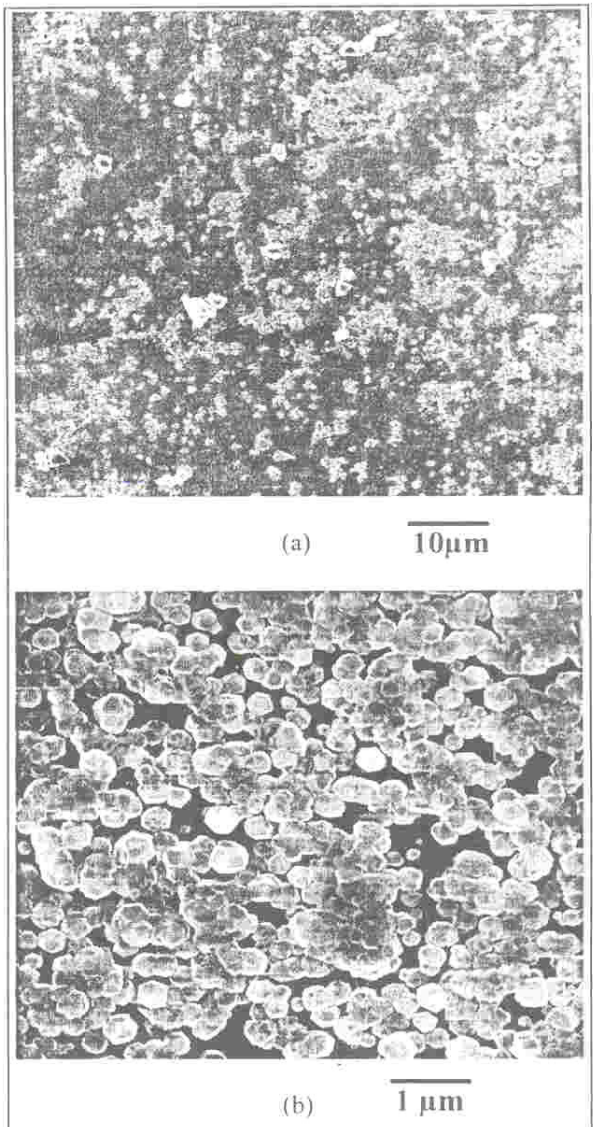

Fig. 2 - SEM micrograph of diamond powder seeded and diamond nucleation particles, a) diamond powder on substrate surface after pre-treatment and b) high density diamond nucleation after 30 minutes of growing.

The dependence of the hardness as a function of post-heating time is shown in figure 3. This hardness increase is very know as a effect of surface hydrogenation [7]. For this reason we established the post-growth heating treatment to promote dehydrogenation and substrate recovery. The dehydrogenation procedure was sufficient to decrease the hardness from 72 to 55 Rockwell-A after 5 hour heating. The hardness as a part of the mechanical properties of the Ti6Al4V substrate was partially recovered.

Normally, diamond film on Ti6Al4V surface with thickness over than 1.0 μm peels off spontaneously during the cooling procedure from the sample that have 72 Rockwell-A hardness. However, up to 5 μm thick diamond films

was reached without peeling off from the sample that have 55 Rockwell-A hardness.

The SEM micrograph of figure 4a shows a good quality diamond film on the 55 Rockwell-A surface, while figure 4b shows the substrate with 72 Rockwell-A surface without film

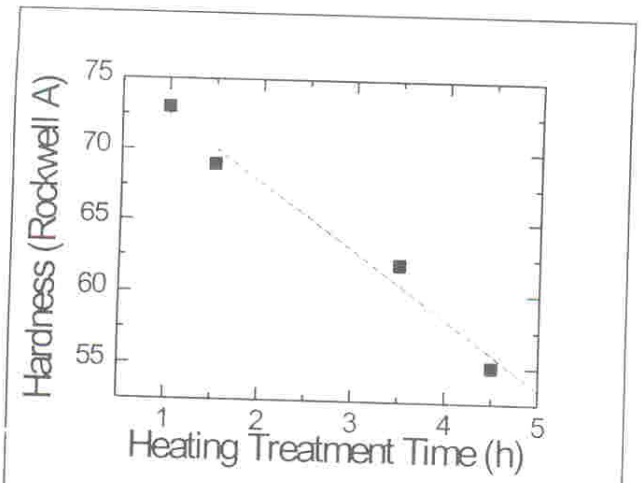

Fig. 3 - Rockwell A hardness surface indentation as a function of heating treatment time after growth in a hot filament reactor.

The micro-Raman scattering spectra of the diamond film in figure 4a is shown in figure 5. A sharp peak close to 1332 cm^{-1}, and also only a small wide band close to 1550 cm^{-1} indicate a good quality film.

Also, EDX analysis on substrate surface showed that the aluminum and vanadium concentration decreases as a function of nucleation time. The aluminum concentration dropped from 6% to under 3%, and vanadium dropped from 4% to under 2%. We speculate that this surface deterioration may influence the film adhesion. These studies will be subject of our future work.

Conclusions

This work showed the effect of the aluminum and vanadium concentration dropping as function of the nucleation time and the restoration of the mechanical properties by dehydrogenation procedure. These effects apparently are as crucial as thermal expansions mismatch in avoiding a good adherence between the diamond film and the Ti6Al4V substrate.

The nucleation enhancement is necessary in order to improve the adhesion between diamond film and the substrate. Diamond powder seeding is a good alternative to improve the nucleation on Ti6Al4V. Also, in situ dehydrogenation procedure after diamond growth was identified as an important technique in order to get film as thick as 5μm on Ti6Al4V substrate.

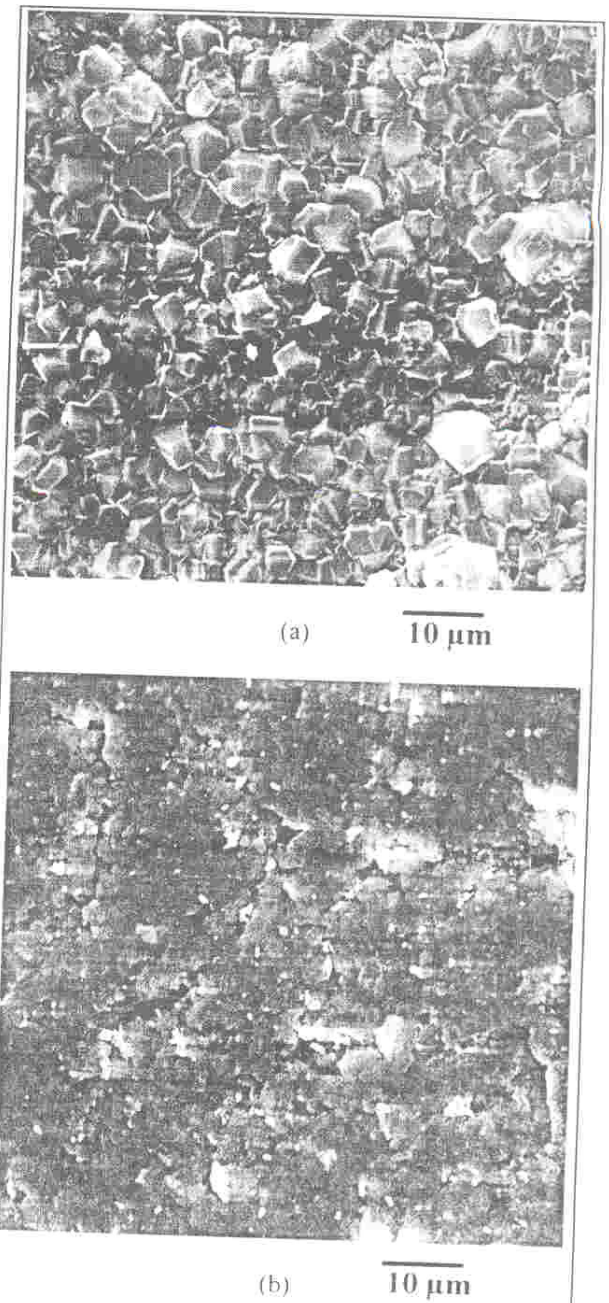

Fig. 4 - SEM micrographs after 2 hour growth: a) Diamond-CVD film on substrate with 55 Rockwell-A hardness and b) Substrate with 72 Rockwell-A hardness without film (it peeled off).

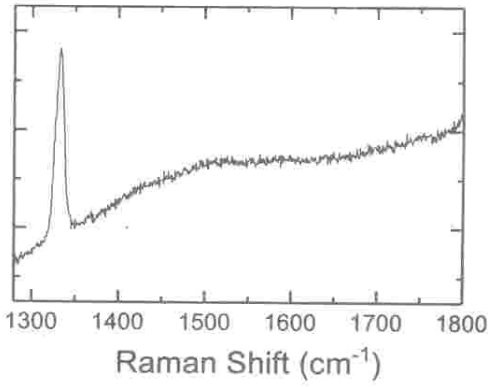

Fig. 5 - Raman Spectra of CVD diamond film on Ti6Al4V substrate.

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