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Application of heat treatment and dispersive strengthening concept in interlayer deposition to enhance diamond film adherence

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Abstract

Two different deposition processes were carried out to enhance adherence of diamond films on WC + 3~5%Co substrate with Ti-Si as the interlayer. One process can be called two-step diamond deposition process. Another process can be called interlayer heat treatment process. Diamond films were deposited by a microwave plasma chemical vapor deposition system. Ti and Si interlayer are deposited by DC sputter and an E-gun, respectively. Film morphologies, interface structure and film quality were examined by SEM, XRD, Auger electron spectroscopy and Raman spectroscopy. The residual stresses and adhesion strengths of the films were determined by Raman spectroscopy and indentation adhesion testing, respectively. Comparing the regular one-step diamond deposition process with the present two different new processes, the average dP/dX values, which are a measure of the adherence of the film, are 354 kgf/mm, 494 kgf/mm and 787 kgf/mm, respectively. In other words, the interlayer heat treatment process gives the best film adherence on average. For the two-step diamond deposition process, the interlayer thickness and the percent diamond surface coverage of the first diamond deposition step are the main parameters, and there exists an optimum Ti thickness and percent diamond coverage for the best film adherence. The main contribution to better film adherence is not a large difference in residual stress, but is due to the following reasons. The interlayer heat treatment can transform amorphous Si to polycrystalline Si, and may form strong TiC and SiC bonding. The polycrystalline Si and the diamond particles from the first diamond deposition step can be an effective seeds to enhance diamond nucleation. Published by Elsevier Science S.A.

Keywords: Diamond films; Heat treatment; Interlayer; Residual stress; Dispersive strengthening

1. Introduction

Diamond is well known for its hardness and wear resistance. Cutting tools protected with diamond films have been produced in the market for several years. However, the major problems of such tools are the poor adhesion and thermal cycling resistance between the film and the substrate due to lack of strong bonding and great internal stress in the films. The origin of the residual stress of diamond films is the intrinsic stress due to the non-diamond carbon content in the films and the thermal stress due to the difference in thermal expansion coefficients between the film and the substrate [1–4]. Another problem of such tools is the use of sintered carbides as the substrate, such as cemented WC substrate; this is due to the fact that the typical binder, Co, for the tools is detrimental to diamond deposition [5–7]. To solve part of the problem, surface etching to minimize Co content on the substrate surface before diamond deposition is generally carried out.

The purpose of this study was to apply heat treatment and the dispersive strengthening concept in Ti-Si brazing alloy deposition as an interlayer between the film and the substrate to minimize the thermal stress of the films and hopefully to develop a strong chemical and mechanical bonding to increase the adhesion of the film.

2. Experimental details

Diamond film deposition on the pretreated substrates was performed by a 5-KW microwave plasma enhanced chemi-

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cal vapor deposition system. The substrate (WC + 3~5% Co) was subjected to the following pretreatments before interlayer and diamond film deposition. It was polished with diamond paste, etched by $HF:H_20$ = 1:1 solution to remove Co from the substrate surface, cleaned and dried. The pretreated substrates were then deposited by two different processes. One process is to use a two-step diamond deposition with Ti-Si as the interlayer, i.e., the dispersive diamond particles were first deposited to cover different percentages of the substrate surface, ranging from 20% to 95%. The samples were then coated with a Ti interlayer and amorphous Si interlayer by DC sputter and an E-gun, respectively, and finally the second step diamond deposition was conducted again. Another process is to use one-step diamond deposition, but the Ti-Si interlayer is subjected to high temperature heat treatment before diamond deposition. The substrate was also pretreated before interlayer deposition. The pretreated substrate was then coated with a Ti interlayer by a DC sputtering system, and with a Si interlayer by an E-gun. Heat treatment of interlayer was carried out at 950°C for 1 h in reducing atmosphere (N_2 + 3% H_2) to transform amorphous Si to polycrystalline Si before diamond film deposition.

The residual stresses of the films were assessed by Raman spectroscopy. In general, a material which is under tensile strain will exhibit a Raman peak which is shifted to lower frequency, while the Raman peak of a material undergoing a compressive strain is shifted to higher frequency. The Raman method has been described in detail elsewhere [1].

The adhesion of the films was determined by the indentation adhesion testing method, which has been described in detail elsewhere [8]. The indentation load, P, versus the diameter of the cracked area, X, was recorded. The slope of the curve, dP/dX, is used as a measure of the quality of adherence between the film and the substrate. A higher value indicates a better adherence.

3. Results and discussion

3.1. Effect of percent diamond surface coverage

For two-step diamond deposition process, the diamond particles or crystallites from the first step diamond deposition occupy only a part of the substrate surface, and are covered by a layer of Ti metal. In other words, Ti interlayer essentially acts as a metal binder to fill up the space between diamond particles to form a metal-matrix composite material. The composite material is expected to be an effective buffer layer for further diamond deposition, and the embedded diamond particles will be an effective seed for further diamond nucleation. The composite material also assumes the advantages of Ti metal in forming a strong TiC bonding on the substrate to increase the film adherence. The Si interlayer was deposited on top of Ti interlayer by E-gun. It is a low temperature physical vapor deposition process, so that the resulting Si films have amorphous structure. The amorphous Si can transform to polycrystalline Si and become the seeds for diamond nucleation during the second diamond deposition step, because the crystalline Si has the same crystal structure as diamond. The typical cross-section morphology at the film-substrate interface is shown in Fig. 1. A very good contact among diamond particles, substrate and Ti-Si interlayer is noted without forming voids at the interface, which are often found in regular diamond or other deposition processes. A better film bonding is expected.

Fig. 2(a, b, c) shows different percent surface coverage of the substrate by diamond particles from the first step diamond deposition process. The corresponding diamond film morphologies after the second step diamond deposition are shown in Fig. 2(d, e, f). It is noted that many diamond crystallites are preferentially nucleated on the diamond seeds from the first diamond deposition step, where the diamond grain size is larger.

The effect of the percent surface coverage by diamond particles from the first step diamond deposition process on residual stress of the films is shown in Fig. 3. It is noted that the thickness of Ti interlayer and the percent diamond coverage have a significant effect on residual stress. At Ti thickness $<$1200 nm, the residual stresses of the films are much greater than with Ti thickness = 2800 nm, except at 95% diamond coverage, where the difference in residual stress is smaller. The residual stresses for this process range from –3.20 GPa to –2.56 GPa, which are comparable with the residual stresses from –3.07 GPa to –2.66 GPa for diamond films without the first diamond particle deposition step. A negative sign indicates a compressive stress.

As to the film adherence, the typical curves of indentation load versus crack length from indentation adhesion testing are shown in Fig. 4. They indicate that adhesion of diamond films for 50% diamond particle coverage is the best in the present deposition conditions, as evidenced by the maximum dP/dX value. The dP/dX values of the films in this

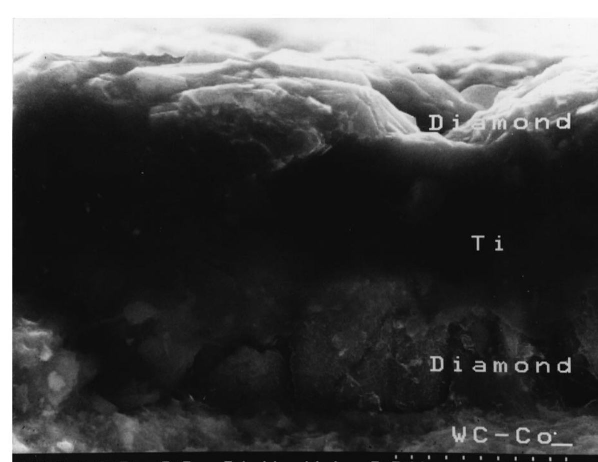

Fig. 1. Interface morphology of diamond film coated WC substrate with Ti-Si interlayer by two-step diamond deposition process (Ti = 2800 nm, Si = 300 nm, 95% diamond coverage of first step diamond deposition).

process range from 268 kgf/mm to 1073 kgf/mm with an average of 494 kgf/mm, which is much greater than the average value of 354 kgf/mm for cases without the first diamond particle deposition step.

3.2. Effect of heat treatment of interlayer

The another process was to use a one-step diamond deposition combined with interlayer deposition and heat treatment processes. The one-step diamond deposition process with Ti-Si films as the interlayer but without heat treatment process was mentioned above, without the deposition of the dispersive diamond particles. The previous paragraph described two-step diamond deposition process without the interlayer heat treatment. The Si interlayer is deposited by E-gun, which is a low temperature physical vapor deposition process, so Si interlayer has amorphous structure. The amorphous Si does not develop a strong bonding with the substrate, and is susceptible to attack by hydrogen atoms during diamond deposition period. However, the amorphous Si may be transformed to polycrystalline Si during the diamond deposition period, or more effectively by heat treatment of this process. It is also known that Si and Ti metals are carbide formers, so heat treatment may cause the forming of strong SiC and TiC bonding to enhance the film adherence. Fig. 5 shows a typical diamond film morphology for heat treated interlayer of 300 nm Ti + 300 nm Si. The corresponding X-ray diffraction pattern for heat treated interlayer before diamond deposition is shown in Fig. 6. A few obvious TiC diffraction peaks are noted, but no SiC peaks, because Si interlayer is insulated from contact with the substrate by Ti interlayer. The results also show that the

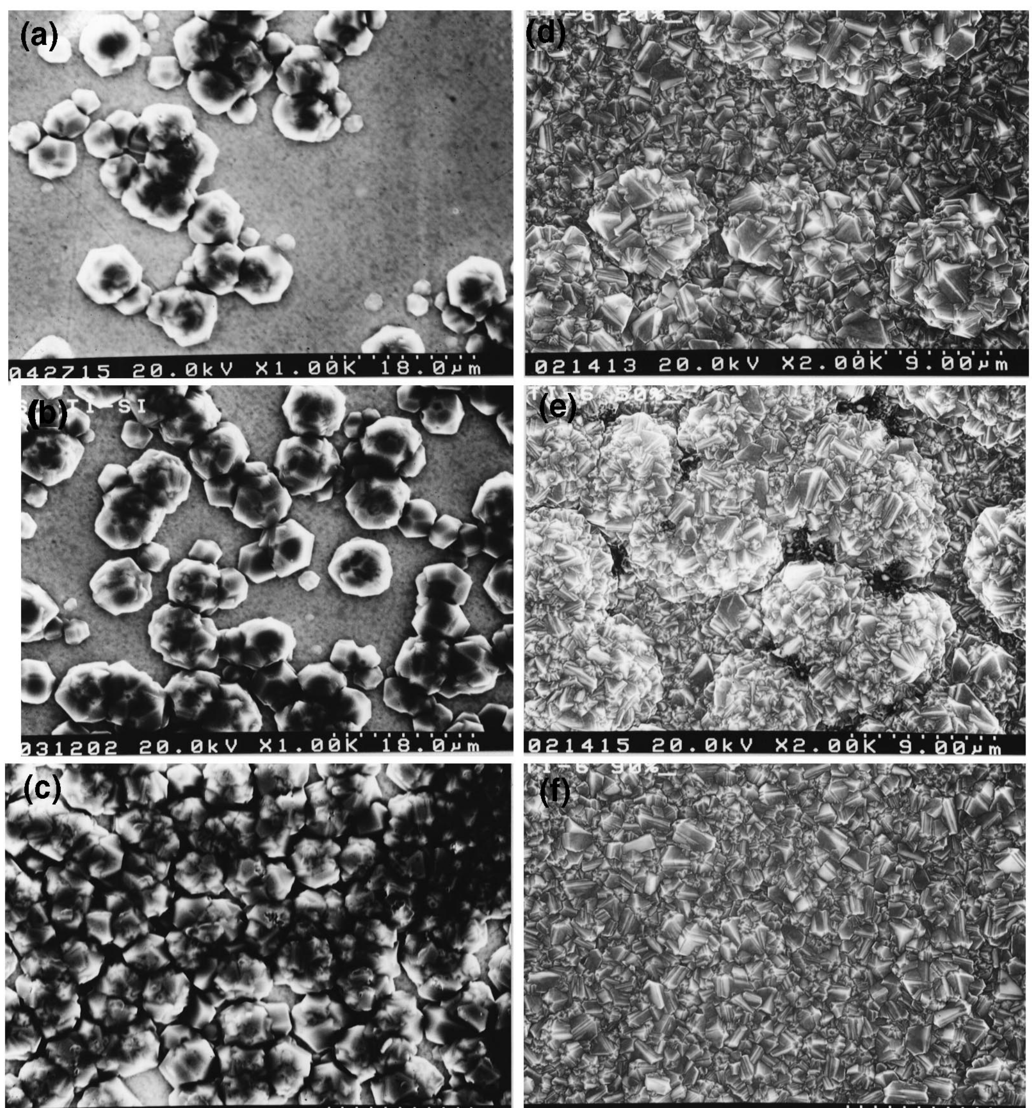

Fig. 2. Surface morphologies of different surface coverage by diamond particles from the first step diamond deposition: (a) 20–30%, (b) 50–60%, (c) 95% diamond coverage. (d), (e), (f) The corresponding surface morphologies of diamond films after two-step diamond deposition.

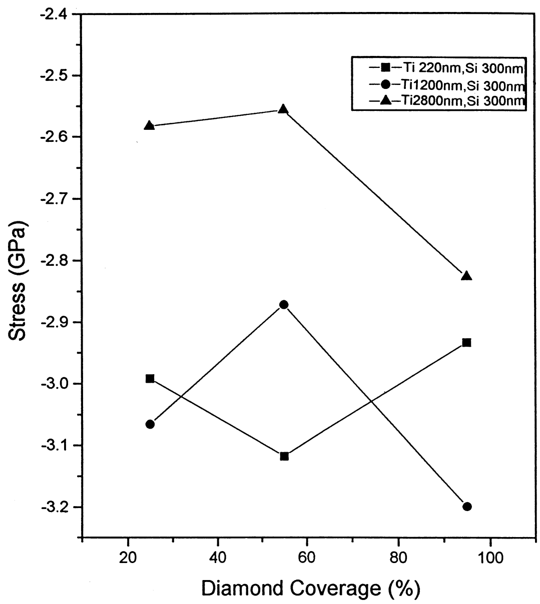

Fig. 3. The residual stresses at different percent diamond coverage and interlayer thickness for two-step diamond deposition process.

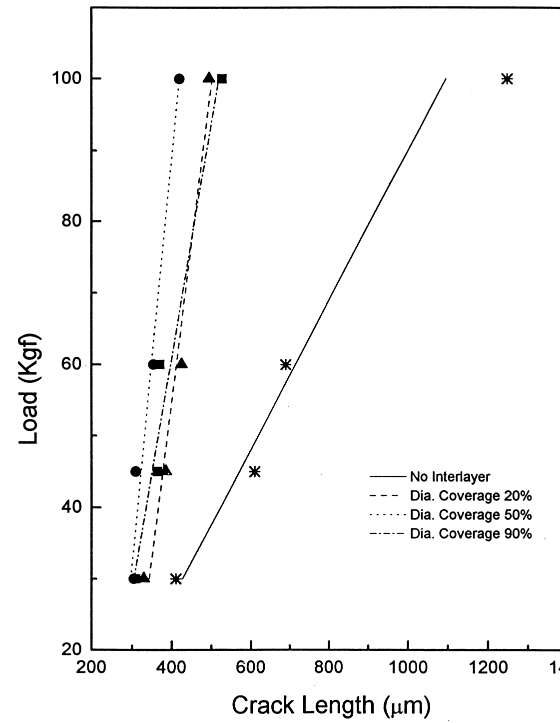

Fig. 4. Typical curves of indentation load versus crack length at different percent diamond coverage for two-step diamond deposition process.

diamond quality for the film in Fig. 5 is better than the corresponding film without heat treated interlayer, as evidenced by a narrower Raman peak around 1332 cm^{-1}.

Regarding mechanical properties, the residual stresses for the films with heat treated interlayer range from −2.90 GPa to −2.64 GPa, which is slightly smaller than the corresponding residual stress for the films without interlayer heat treatment. Typical curves of indentation load versus crack length for diamond films with heat treated interlayer are shown in Fig. 7. The dP/dX values range from 376 kgf/mm to 1437 kgf/mm with an average of 787 kgf/mm, which is even greater than that of the two-step diamond deposition process. This may be due to the fact that heat treated interlayer results in a transformation of amorphous Si to polycrystalline Si, in addition to forming TiC and SiC bonding to enhance film adherence; the crystalline Si has the same crystal structure as diamond crystal, so it favors diamond nucleation and bonding.

The fractured surface was also examined by Auger electron spectroscopy (AES). The results show obvious Ti and Si signals on both substrate side and film back side of the fractured sample, but no Co signal. This signifies that Ti + Si interlayer can effectively inhibit the detrimental effect of Co in the substrate on diamond nucleation. The detailed AES carbon signals for substrate side, film back side and film front side of the fractured sample are shown in Fig. 8(a, b, c, respectively). By comparing various carbon peak patterns of Williams and Glass [9], carbon signal from

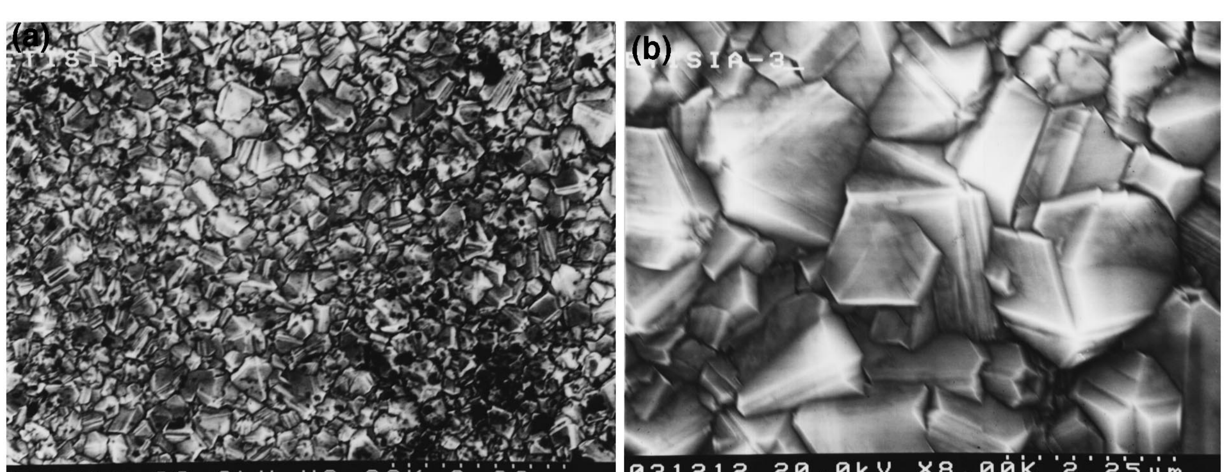

Fig. 5. Typical morphology of diamond films for the interlayer heat treatment process (Ti = 300 nm, Si = 300 nm).

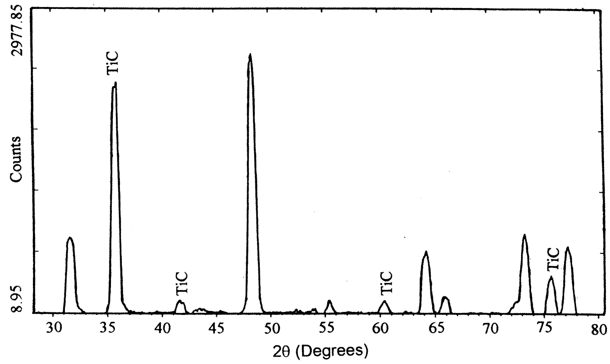

Fig. 6. X-ray diffraction pattern of the Ti-Si coated substrate after 950°C, 1-h heat treatment before diamond deposition.

the film back side is identified to be graphite and carbide. It may signify that graphite is formed at the initial stage of diamond deposition. This is in agreement with other investigators [10,11]. The results are also in agreement with the statement that Ti-Si interlayer may form strong TiC or/and SiC bonding to enhance the film adherence.

4. Conclusions

Diamond films were deposited on the cemented WC + 3~5% Co substrates by two different processes. One process used a two-step diamond deposition process with Ti-Si as the interlayer. Another process was the regular one-step diamond deposition process, but the interlayer was

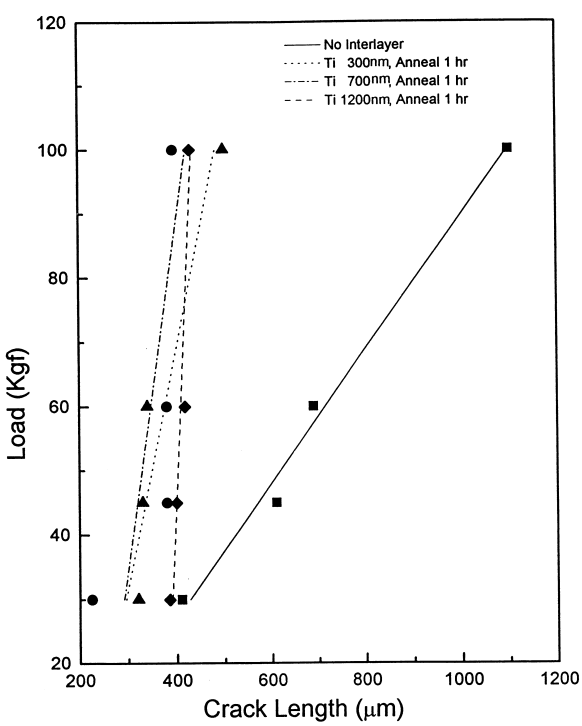

Fig. 7. Typical curves of indentation load versus crack length at different interlayer thicknesses for the interlayer heat treatment process.

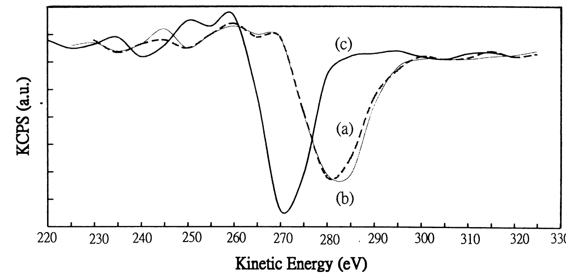

Fig. 8. Auger electron spectra for the fractured sample deposited by the interlayer heat treatment process (a) on the substrate side, (b) on the film back side, and (c) on the film front side.

subjected to high temperature heat treatment before diamond deposition. The experimental results show the following conclusions.

1. For the two-step diamond deposition process, the interlayer thickness and the percent surface coverage of diamond particles from the first step diamond deposition can have a significant effect on film adherence. The results show that there exists an optimum percent surface diamond coverage (around 50%) for the best film adherence. In the present deposition conditions, the film with the highest Ti thickness of 2800 nm, 300 nm Si and a 50% diamond surface coverage results in smaller film residual stress and the best film adherence of 1073 kgf/mm.

2. Comparing three different processes with the same Ti-Si interlayer, i.e., one-step diamond deposition process, two-step diamond deposition process, and one-step diamond deposition with heat treated interlayer, the average dP/dX values for the three different processes are 354 kgf/mm, 494 kgf/mm and 787 kgf/mm, respectively. However, in general there are no significant differences in residual stress of the films. The reasons may be as follows. Ti and Si are a good carbide formers, forming strong TiC and/or SiC bonding to enhance the film adherence. The amorphous Si may be transformed to polycrystalline Si during diamond deposition period or more effectively by heat treatment before diamond deposition, and the polycrystalline Si has the same crystal structure as diamond, which can act as seeds for diamond nucleation. In the case of two-step diamond deposition process, the diamond particles produced in the first step will be effective seeds for the second step diamond nucleation, and the diamond particles embedded in the Ti metal matrix can form a dispersive strengthening structure to enhance the toughness of the interlayer and also act as an effective buffer layer.

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