



INTRINSIC STRESS DEVELOPMENT IN Ti-C:H CERAMIC NANOCOMPOSITE COATINGS

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ABSTRACT

The development of intrinsic stresses within titanium-containing hydrocarbon (Ti-C:H) coatings was monitored by in-situ substrate curvature measurements using a multi-beam optical sensing (MBOS) technique. Stress as a function of the Ti-C:H layer thickness was monitored in a wide range of specimens, from nearly pure amorphous hydrocarbon (a-C:H) to nearly pure titanium carbide (TiC). The intrinsic stress within Ti-C:H was found to vary significantly in magnitude and depend systematically on the Ti composition.

Ti-containing hydrocarbon (Ti-C:H) coatings, consisting of a nm-scale mixture of crystalline titanium carbide (TiC) and amorphous hydrocarbon (a-C:H)¹, form a prototype of pseudo-binary ceramic nanocomposites. Ti-C:H coatings possess mechanical properties and tribological characteristics which depend systematically on coating composition², demonstrating the potential of engineering ceramic nanocomposite coatings for specific applications. The dependence of tribological characteristics of Ti-C:H coatings on the Ti composition has been related to a percolation type transition³. In addition to the influence of plasma characteristics, the coating composition may therefore exert a significant influence on intrinsic stress development within ceramic nanocomposite coatings.

This paper addresses the dependence of intrinsic stresses within Ti-C:H coatings on the Ti composition. Ti-C:H deposition was accomplished using a high-density plasma assisted hybrid chemical vapor deposition (CVD)/physical vapor deposition (PVD) process. Under nominally identical plasma conditions, a series of Ti-C:H coatings, ranging from nearly pure a-C:H to nearly pure TiC, was deposited onto Si(100) substrates. The development of intrinsic stresses was monitored by in-situ measurements of substrate curvature change. Our results show that the intrinsic stress within Ti-C:H coatings depends systematically on the Ti composition. A significant increase in stress was observed as the Ti composition increases beyond 30 at. % and suggested to be related to the percolation type transition in the coating microstructure.

Details of experimental setup and procedures will be described in the presentation.

Figure 1 shows a typical substrate temperature – time history during a complete Ti-C:H deposition run. The Ti cathode current was 1.0A during Ti-C:H deposition. During the etch and cool stages, the substrate temperature rose from ~ 25 °C to ~ 225 °C and fell to ~ 150 °C. It stayed ~ 150 °C during Ti interlayer deposition, and rose to ~ 225 °C during Ti-C:H deposition. During the entire deposition run, the temperature difference between front and back beam surfaces was ≤ 5 K. Such a temperature difference across a 300 μm thick Si wafer would induce a substrate curvature change ΔK of $\sim 1/21 \text{ m}^{-1}$. Figure 1 shows that, during Ti interlayer and Ti-C:H deposition, change in relative reflected laser spot spacing $\Delta D/D_0$, which is measured experimentally and linearly related to the curvature change, induced by temperature gradient across the Si substrate is substantially smaller than 10 %.

A multitude of Ti-C:H/Ti/Si(100) specimens were deposited. During each deposition, the curvature change of the Si(100) beam substrate was monitored by MBOS. Figure 2 shows the average composition of the Ti-C:H layers as a function of the Ti cathode current obtained by combining RBS and ERD measurements. The Ti and hydrogen compositions respectively increase and decrease in a monotonic fashion with increasing Ti cathode current. The observed trend is consistent with our previous results and supports the fact that Ti-C:H coatings are pseudo-binary TiC/a-C:H nanocomposites, in which hydrogen inclusion occurs only through incorporation into the a-C:H phase⁴. Figure 3 shows measured $\Delta D/D_0$ during Ti-C:H deposition as a function of time. The time origin coincides with the beginning of Ti-C:H deposition. Only the curvature change due to Ti-C:H deposition is taken into account, as $\Delta D/D_0$ was set to zero at time zero. In the early stage of growth, 0 – 400 sec, $\Delta D/D_0$ increases approximately linearly to ~ 30%, independent of the Ti composition. In the late stage, 400 – 2500 sec, $\Delta D/D_0$ continues to increase linearly with time, but in most cases with a distinctly different slope as compared to the early stage.

Temperature measurements, such as the one shown in Figure 1, showed that during the early stage of Ti-C:H growth, the substrate temperature rose ~ 70 K. In the late stage, the substrate temperature change was ≤ 25 K at all Ti cathode currents. This temperature change ΔT would induce a substrate curvature change ΔK_T due to the difference in thermal expansion between Si and the Ti-C:H coating $\Delta\alpha_{s-c}$,

$$\frac{Y_s t_s^2}{6} \Delta K_T = Y_c \Delta a_{s-c} t_c \Delta T,$$

where Y_s , t_s , Y_c , and t_c are respectively the biaxial modulus and thickness of the substrate and the coating. $\Delta\alpha_{s-c}$ was taken to be $\sim -4 \times 10^{-6} \text{ K}^{-1}$, according to measurements on W-C:H coatings⁵. For the present measurements, a conservative estimate yielded $\Delta D/D_0 \leq +5\%$ for $\Delta T = +100 \text{ K}$ ⁶. It is thus concluded that thermal contribution to the present measurements can be neglected, and that in all cases the measured $\Delta D/D_0$ reflects intrinsic stress development. The linear dependence of $\Delta D/D_0$ on time during late stage growth indicates a constant level of incremental intrinsic stress as the Ti-C:H layer thickens.

In summary, a detailed experimental study of the dependence of intrinsic stress within Ti-C:H coatings on the Ti composition was performed by measuring in-situ substrate curvature change. The intrinsic stress within Ti-C:H layers was found to vary significantly in magnitude and depend systematically on the Ti composition. The observed stress dependence on coating composition is suggested to correlate with a percolation type transition in the coating microstructure, and may be one generic characteristic of ceramic nanocomposite coating systems.

ACKNOWLEDGMENTS

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FIGURES AND TABLES

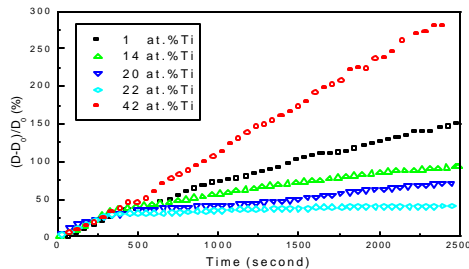


Figure 3. Changes in reflected spot relative spacing from Si(100) beam substrates during Ti-C:H deposition for several Ti-C:H coatings of various Ti compositions.

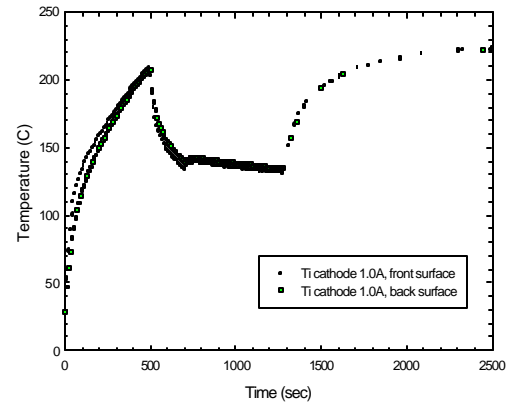


Figure 1. Temperature – time history during an entire Ti-C:H deposition run: 0 – 500 sec, substrate etching; 500 – 700 sec, cool down; 700 – 1300 sec, Ti interlayer deposition; 1300 – 2500 sec, Ti-C:H deposition.

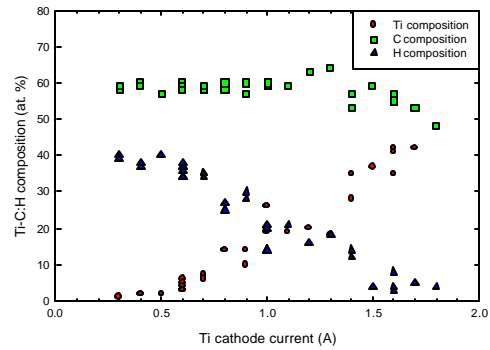


Figure 2. Composition of Ti-C:H coatings as a function of the Ti cathode current during deposition.

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4. D. M. Cao, B. Feng, W. J. Meng, L. E. Rehn, P. M. Baldo, M. M. Khonsari, *Appl. Phys. Lett.* **79**, 329 (2001).
5. J. S. Wang, Y. Sugimura, A. G. Evans, W. K. Tredway, *Thin Solid Films* **325**, 163 (1998).
6. For the present Si(100) beam substrates, $Y_s = 180 \text{ GPa}$ and $t_s = 300 \mu\text{m}$. t_c is taken to be 800 nm, the entire thickness of the Ti-C:H layer. The maximum biaxial modulus for Ti-C:H coatings is $\sim 180 \text{ GPa}$ (ref. 8), thus Y_c is taken to be 180 GPa.