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# Hard Yet Tough Ceramic Coating: Not a Dream Any More—I. Via Nanostructured Multilayering

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This paper describes how hard yet touch ceramic coating is achieved: hard and brittle nanocomposite layers (nanocrystalline CrAlN imbedded in amorphous $SiN_x$ or nc-CrAlN/a-$SiN_x$) are intimately combined with soft and tough CrAlN polycrystalline layers (pc-CrAlN) to build multilayer coatings of different period thickness with a constant total coating thickness of one micron. At the period thickness of 20 nm, an improved hardness of 33 GPa was achieved with a scratch toughness 5 times as much as that of the nanocomposite monolayer. At the period thickness of 40 nm, drastic scratch toughness was increased 7 folds at a slightly reduction of hardness (from 30 to 27.9 GPa).

**Keywords:** Multilayers, Hard Yet Tough, TEM, CrAlSiN.

## 1. INTRODUCTION

Toughened hard ceramic coatings are much desired for practical industrial applications but seldom achieved. This paper utilized a hard nanocomposite coating (i.e., nc-CrAlN embedded in a-$SiN_x$) as one layer and a much softer but much tougher polycrystalline CrAlN (or, "pc-CrAlN") as the neighboring layer to construct a novel nanostructured multilayer coating. Nanoindentaion and micro-scratch tests revealed that with this architecture, hard yet tough coatings could be produced.

## 2. EXPERIMENTAL SETUP

The deposition of the coatings was conducted via co-sputtering of Cr, Al and Si targets (all are 6 inch in dia. 99.99 at.% in purity) on Si (100) wafer and mirror-finishing stainless steel 420 (SUS420) substrate in mixed Ar and $N_2$ ambient. The processing pressure was maintained at 0.4 Pa with Ar flow rate of 40 sccm and $N_2$ flow rate of 20 sccm. During the deposition, the substrate temperature was kept at 400 °C.

The power density on the Cr, Al and Si (radio frequency, 13.67 MHz) targets were set at 1.5 W/cm$^2$, 2.2 W/cm$^2$ and 4.1 W/cm$^2$, respectively. The radio frequency (r.f.) induced negative bias was set at 160 V. The thickness of one period (i.e., one layer of nanocomposite plus one layer of pc-CrAlN, denoted as $\Lambda$) of the multilayer varied from 10, 20, 40 and 60 nm. The thickness ratio of sub-layers was controlled at 1:1 with 1 $\mu$m total thickness. Negative substrate bias of 160 V was applied to pre-clean the contaminants clinging on the surface. Monolayer pc-CrAlN and nanocomposite of 1 $\mu$m thickness were also deposited for comparison.

The chemical composition was evaluated using Field Emission Electron Probe Micro-Analyzer (FE-EPMA, JEOL JXA-8500F). The cross-sectional microstructures, such as the interface and period thickness, were investigated using Transmission Electron Microscopy (TEM, JEOL JEM-2100F). Hardness was measured using a nanoindentation (Hysitron TI-900 TriboIndenter) with a Berkovich diamond probe. Maximum indentation depth was set at 80 nm, less than one tenth of the coating thickness to minimize the substrate effect.

Toughness evaluation of ceramic coatings and films is still a challenging endeavor.[1]

In this study, Scratch Crack Resistance was used to characterize the toughness of the coatings.[2] The value of "Scratch Crack Resistance" was evaluated through a micro-scratch test (J&L Tech. Scratch Tester) on the

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**Table I.** Chemical composition of pc-CrAlN, nanocomposite monolayer and multilayers.

| | | Concentration (at.%) | | | | |
|---|---|---|---|---|---|---|
| Code | Bilayer thickness (nm) | Cr | Al | Si[a] | N | O |
| pc-CrAlN | — | 28.5 | 17.4 | — | 52.7 | 1.4 |
| Nanocomposite | — | 21.4 | 13.5 | 8.5 | 55.3 | 1.3 |
| mt-10 | 10 | 26.1 | 15.4 | 4.1 | 54.2 | 0.2 |
| mt-20 | 20 | 26.5 | 15.0 | 4.2 | 54.1 | 0.2 |
| mt-40 | 40 | 26.3 | 15.1 | 4.2 | 54.1 | 0.3 |
| mt-60 | 60 | 26.3 | 15.5 | 4.1 | 53.9 | 0.2 |

[a]Chemical content is evaluated from the coatings throughout the thickness.

coatings deposited on SUS420 substrates. Applied linear load was set at 0–50 N. The scanning length was set at 5 mm with scanning speed of 0.08 mm/s. The load at which an ultrasonic signal first emitted was regarded as the lower critical load ($L_{c1}$) of the onset of cracking. And the load accompanied with a sudden change of coefficient of friction was regarded as the higher critical load ($L_{c2}$) corresponding to coating spallation.[3,4] The product of $L_{c1}$ and ($L_{c2} - L_{c1}$) was then defined as scratch Crack Propagation Resistance ($CPR_s$) to describe the resistance of a coating to crack propagation under the scratch testing.

## 3. RESULTS

### 3.1. Chemical Composition and Microstructure

The chemical compositions of the monolayer and the multilayers are summarized in Table I. All the elemental content are average value determined throughout the coating thickness. Therefore, the Si content in nanocomposite sublayer should be around 8 at.% by considering the thickness ratio (1:1) in one period.

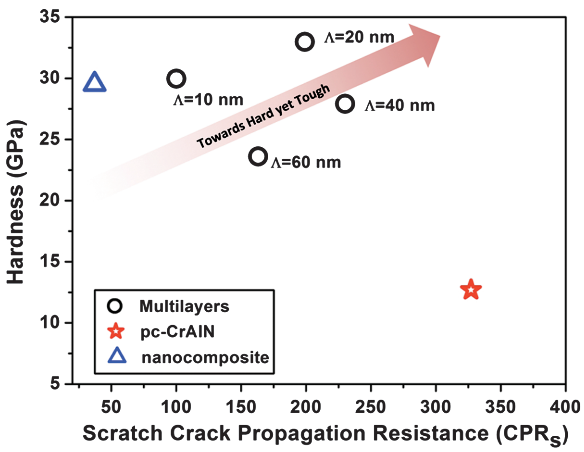


**Fig. 2.** Hardness versus "toughness" (scratch crack propagation resistance) of the coatings.

Microstructure of multilayers with bilayer thickness of 20 nm is seen in Figure 1(a). pc-CrAlN and nanocomposite layers are clearly illustrated (Fig. 1(b)). The bilayer thickness is confirmed as designed. However, the layer interface is not ideally sharp due to the diffusion of the Si from the nanocomposite into the neighbored layers. In the nanocomposte sub-layer, the size of the nanocrystalline CrAlN is around 5 nm (inset of Fig. 1(b)), while the grain size in pc-CrAlN is aroud 10 nm (Fig. 1(b)). Further study of the microstructure is on the way and pending to be explored.

### 3.2. Hardness and Toughness

Figure 2 plots nanoindentation average hardness versus scratch toughness. It is obvious that the pc-CrAlN

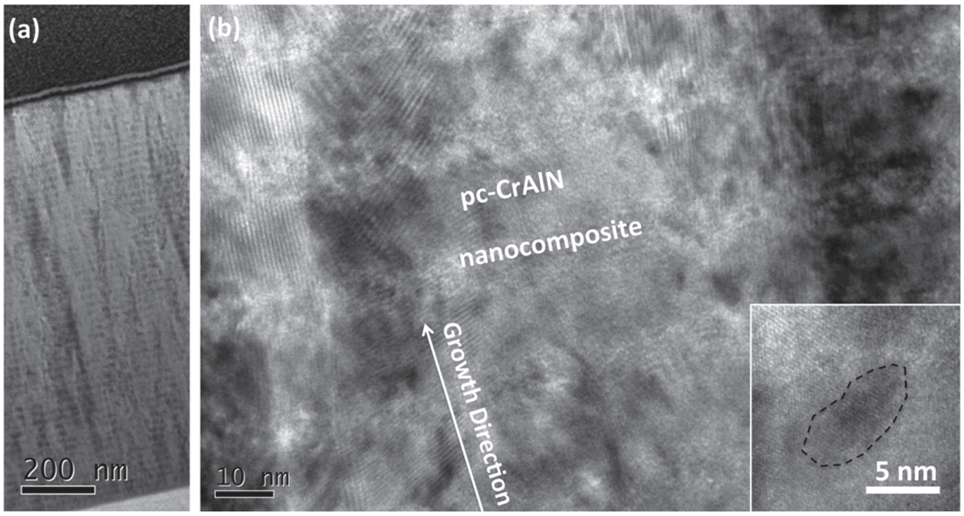


**Fig. 1.** (a) TEM overview of the multilayer coating with period thickness of 20 nm, (b) a close-up TEM image of (a), inset is the enlarged partition of nanocomposite (i.e., nc-CrAlN in a-$SiN_x$) layer with nanograin size of ~5 nm.

monolayer is tough but soft (the star at the lower right corner), whereas the nanocomposite monolayer is hard but very brittle (the open triangle at top left). Ideally, top right corner is the best, i.e., hard yet tough. The multilayer coatings (the open circles), do appear toward that direction in varying extent at varying period thickness: at $\Lambda = 10$ nm, the hardness of the multilayer coating matches that of the nanocomposite monolayer, meanwhile, its toughness is better (moving towards right in the Hardness vs Toughness space). At even larger period thickness, $\Lambda = 60$ nm, the multilayer's hardness drops with increased toughness; at $\Lambda = 40$ nm, hardness returns with much improved toughness (7 times as much as that of nanocomposite monolayer); at $\Lambda = 20$ nm, the hardness further improves, and even surpass that of the nanocomposite (from less than 30 to 33 GPa) at a slight drop in toughness from that at $\Lambda = 40$ nm. At this architecture ($\Lambda = 20$ nm), the multilayer coating's toughness increased 5 folds from that of the hard nanocomposite (the open triangle).

## 4. CONCLUSIONS

With proper design of period thickness $\Lambda$, hard yet tough ceramic coating is achieved through multilayering structure: At $\Lambda = 20$ nm, toughness of the coating increased 5 folds together with some hardness enhancement (from less than 30 to 33 GPa). At $\Lambda = 40$ nm, the toughness increased 7 folds with a slight decrease of hardness (from 30 to 27.9 GPa).

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