Grain boundary strengthening of carbon-doped TiZrN coatings by laser carburization

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ABSTRACT
The improved mechanical properties of carbon-doped TiZrN coatings were investigated in terms of the microstructure and bonding state. The carbon incorporation and structural change were confirmed as a shift to lower degree of the diffraction pattern and the decreased grain size from 24.64 to 22.19 nm. The clear grain boundaries (GBs) were observed in the carbon-doped coating, and its fast Fourier transform (FFT) exhibited a diffused ring pattern. Edge dislocations were also observed in the inverse FFT image, indicating the formation of an amorphous phase due to laser carburization. From the X-ray photoelectron spectroscopy depth profile analysis, the carbon concentration decreased to 37.26 at.% after carburization, which is non-stoichiometric behavior that suggests the formation of the amorphous carbon (a-C) rather than carbides. Both sp²- and sp³-hybridized bonds were detected in the C 1s spectrum of the carbon-doped coating, indicating that the diffused carbon atoms were trapped in the GBs as a-C. The change in the GB structure increased the compressive residual stress from 3.97 to 4.63 GPa. In addition, the hardness, elastic strain to failure (H/E), and plastic deformation resistance (H/E) of the carbon-doped TiZrN increased by 19.22%, 12.64%, and 49.59%, respectively, demonstrating the effect of GB strengthening.

1. Introduction
The machining industry has shown great interest in developing high-performance coatings to improve tool life, high quality, and lower costs [1,2]. The excellent properties of transition metal nitride coatings are sufficient to meet the expectations of industry [2–5]. Titanium nitride (TiN) is widely used because of its superior wear and corrosion resistances. Ternary metal nitrides, such as TiZrN and TiAlN, have attracted considerable attention, and high hardness has been achieved by controlling the concentration of solute metal ions [6,7]. In particular, the good thermal properties of TiZrN might be suggested as one of the solutions for the heat generated during wear [8,9].

An increase in hardness can lead to a high performance, but high hardness can cause a decrease in damage resistance [10]. For coatings requiring good damage resistance, a fine columnar structure has an advantage over a dense equiaxed grain structure [11,12]. In the columnar structure, intergranular shear sliding under an external load reduces the stress concentration [12,13]. An amorphous phase was introduced into the grain boundary to further improve the resistance to shear deformation [14,15]. The amorphous carbon (a-C) and silicon phases formed on the grain boundaries of (Ti,Si)(C,N) caused a difference in interfacial energy and led to a high hardness and low friction coefficient [16]. M. Stueber et al. reported an improvement of the mechanical properties due to the a-C network in (Ti,Al)(N,C) [17]. Therefore, it is necessary to understand the influence of structural evolution on the mechanical properties of the coatings.

This work studied the composition and nanostructure of carbon-doped TiZrN coatings to explain the variation of the mechanical properties and damage resistance. The crystallographic changes due to the doped carbon were confirmed by the diffraction patterns and the assumption of an intergranular structure. The structural evolution was observed using electron microscopy, and the bonding state of the doped carbon was analyzed using photoelectron spectroscopy. The elastic modulus and hardness measured by the nanoindenter were used to calculate the change in the residual stress and to investigate the role of carbon in the mechanical properties.

2. Experimental procedure
Stainless steel 304 (SUS304) was employed as a substrate due to its corrosion resistance [18,19]. TiZrN coatings were deposited by RF/DC magnetron
sputtering on a SUS304 substrate at 723 K for 6 h using a titanium zirconium target with an equal weight ratio (50:50 wt.%, 99.99% purity). Surface contamination of the substrates was eliminated by ultrasonic wave cleaning with ethanol before deposition. The carbon paste for carburization was composed of graphite powder (Alfa Aesar), polyvinylidene fluoride (Merck) as a binder, and N-methyl-2-pyrrolidone (Merck) as a solvent. The substrate was covered with the paste and dried at 343 K. The carbon-doping process was conducted using an Nd:YAG pulsed laser ablation system (LSX-213, CERAC Technologies) with a wavelength of 213 nm and an energy output of 40%. After carbon doping, the paste was removed with ethanol and acetone.

The structure and phase composition of the samples were assessed by X-ray diffraction (XRD, EMPYREAN, PANalytical B.V.) with Cu Kα radiation at the KBSI Daegu Center. Grazing-incidence XRD (GIXRD, EMPYREAN, PANalytical B.V.) with Cu Kα radiation at an incident angle of 1° was conducted to analyze the structural changes after laser carburization. The average grain size was calculated from Scherrer’s formula using the XRD patterns. Cross-sections of the samples were prepared using a focused-ion beam (FIB), and the microstructure was observed in more detail using transmission electron microscopy (TEM, JEM-2100 F, JEOL) at the KBSI Busan Center. The TEM micrographs were processed using Digital Micrograph software (Gatan Inc.) to obtain fast Fourier transform (FFT) patterns and inverse FFTs. X-ray photoelectron spectroscopy (XPS, ESCALAB250, VG scientific) was used to characterize the chemical bonding of the specimens. The neutral adventitious C 1s peak at 284.6 eV was used as a reference for the binding energies. A nanoindenter (HM2000, Fischer Technology Inc., Windsor) equipped with a Berkovich indenter (tip radius of 5 μm) was used to determine the hardness (H) and Young’s modulus (E) of the coatings. To minimize the effect of the substrate, a peak load of 5 mN was applied, and the indenter did not penetrate more than 10% of the total coating thickness. A mean value was obtained from 30 indentation tests. The residual stress was calculated based on the relationship between the residual stress (σr) and contact radius (a0) at the onset of yielding, which is given as following [20].

\[
\frac{\sigma_r}{\sigma_y} = 1 - \frac{1.26}{\pi} \frac{E \cdot a_0}{\sigma_y R}
\]

where σy is the yield stress, which is assumed to be one-third of the hardness [21], and R is the radius of the indenter.

3. Results and discussion

Figure 1 shows the XRD and GIXRD patterns of the TiZrN coatings before and after carbon doping. As shown in Figure 1a, both coatings exhibited peaks corresponding to the TiZrN phase, and the (111) plane was the preferred orientation, indicating a columnar grain structure. However, the slight peak shift to lower angles in the carbon-doped coating suggests that there was a solid solution effect due to incorporation of carbon atoms [22,23]. The grain sizes of the TiZrN coatings before and after carbon doping were calculated from the (111) plane using Scherrer’s formula. The grain size decreased from 24.64 to 22.19 nm after carbon doping, indicating that the incorporated carbon influences the intergranular structure. The penetration depth of grazing incidence X-ray beam with the incidence angle of 1° was expected about 150 nm, as surface-sensitive analysis [24]. As shown in the GIXRD pattern of the carbon-doped
coating in Figure 1b, a slight carbon (002) plane was detected, confirming the formation of a carbon phase after laser carburization. A peak shift of TiN and ZrN planes to lower angles also detected after carburizing. It indicates that the solid solution effect by the carbon incorporation corresponding to the XRD pattern.

Figure 2 shows the structural changes in the TiZrN coatings before and after carbon doping. The microstructural characterization using FIB and high-resolution TEM showed that clear boundaries were present in the coating after laser carburization, as shown in Figures 2a and 2d. The dark grains in the carbon-doped specimen display a high density of crystalline defects, and may originate from the increased residual stress [25]. The FFT patterns in Figures 2b and 2e show the change from a distinct dot pattern to a diffused ring pattern, suggesting the formation of an amorphous phase. In the images filtered by the inverse FFT patterns using the corresponding FFT patterns (Figures 2c and 2f), a uniform lattice with almost no defects was observed before carburization, while numerous defects in the form of edge dislocations were observed after carburization [26]. The edge dislocations indicated the presence of an amorphous phase and lattice strain, which limits plastic deformation and dislocation movement [26,27].

XPS depth profiling was performed to determine the carbon composition from the surface to a depth of 150 nm. The doped carbon diffused to more than 150 nm from the surface, and its concentration gradually decreased to 37.26 at.% as shown in Figure 3a. The carbon concentration was still higher than that of the existing nitrogen at 150 nm. This non-stoichiometric behavior suggested that the carbon formed other bonds, such as those in amorphous carbon (a-C) [28].

To analyze the bonding states of the doped carbon, the XPS spectra at the surface and at 150 nm were obtained, as shown in Figure 3b. Both sp²- and sp³-hybridized bonds were detected at approximately 284.8 and 285.1 eV, respectively, indicating the formation of a-C in the carburized layer [29]. The a-C can be formed by trapping carbon atoms diffused by short-circuit diffusion in grain boundaries (GBs), and the Cottrell atmosphere is easily formed by the a-C. The sp³-hybridized bond was preferred for bonding formation as it is more stable and has a shorter bonding
length. The carbide (TiC or ZrC) peak around 283 eV confirmed the presence of substitutional carbon or the occupation of vacancies by some diffused carbon atoms. This revealed that the diffusion type of the carbon atoms is Harrison Type-B in short-circuit diffusion types [30,31]. It was assumed that the larger carbide at a depth of 150 nm was formed as the effect of Cottrell atmosphere on the supersaturated carbon from GBs.

The CF₂ peak was due to fluorine in the binder used in the carbon paste, and a slight oxide peak was generated owing to oxidation during the carbon doping process [32,33].

Figure 4 shows the compressive stress in the TiZrN coatings before and after carburization. The residual stress was calculated using Equation 1 and increased by approximately 43% with the incorporation of carbon. The residual stress in the coating can be caused by a mismatch in the coefficient of thermal expansion and structural defects, such as atom incorporation in the GBs [34,35]. In this study, the strain energy generated by GB trapping of doped carbon may not be sufficiently released, which can explain the existence of edge dislocations in the inverse FFT pattern.

The indentation loading and unloading curves of the coatings are shown in Figure 5a and are summarized in Table 1. Both exhibited elastic–plastic deformation, and the penetration depth decreased with the formation of the carburized layer. The total energy and plastic energy during each indentation cycle are the area under the load curve and the area surrounded by the loading and unloading curves, respectively. The area excluding the plastic energy from the total energy is the elastic energy area, and the resilience was calculated as the ratio of elastic energy to the total energy. The carbon-doped coating showed a high deformation resistance, with a resilience of 44.66%. The hardness increased by 19.22% (from 32.41 to 38.64 GPa), and the Young’s modulus increased by 6.33% (from 372.23 to 395.80 GPa). Using the measured hardness and Young’s modulus, the elastic strain to failure (H/E) and plastic strain resistance (H/E²) were calculated. The carbon-doped coating exhibited an increase of 12.64% in H/E and 49.59% in H/E².

The improved mechanical properties of the carbon-doped TiZrN coating can be explained by the intergranular structure, as shown schematically in Figure 5b. Previous results indicated that grain boundary strengthening occurred due to the formation of a-C through the short-circuit diffusion of carbon. Thus, grain boundary strengthening is the main strengthening mechanism rather than solid solution strengthening.

4. Conclusion

In this paper, the mechanical properties of carbon-doped TiZrN coatings were studied in terms of their structural evolution and bonding environment. The grain size of the TiZrN coating decreased from 24.64 to 22.19 nm after carburization, indicating a change in the intergranular structure. It was found that the solid solution effect by the carbon incorporation, becaused
of the peak shift to lower diffraction angles. The microstructure of the carbon-doped TiZrN exhibited clear boundaries and dark grains, suggesting the high density of crystalline defects and the origin from the increased residual stress. The FFT patterns changed from a dot pattern to a diffused ring pattern, implying the formation of a disordered phase. In the inverse FFT image of the carbon-doped TiZrN, the formation of an amorphous phase was also displayed by the formation of edge dislocations. XPS depth profile analysis indicated that doped carbon diffused up to approximately 150 nm below the surface and exhibited non-stoichiometric behavior as a signal of a-C. Both sp²- and sp³-hybridized bonds were detected because of the formation of a-C from carbon atoms trapped in the GBs. The supersaturated carbon from GBs might actively react at the depth, due to the Cottrell atmosphere by a-C. The compressive residual stress increased by 16% owing to the a-C located at the GBs. Improvements in hardness (~19%), elastic strain to failure (~12%), and plastic deformation resistance (~49%) were achieved owing to the strengthening effect of the a-C in the GBs.

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Disclosure statement

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