

A comparative study of thermal shock tests : chemical composition and microstructural analyses on the surface of TiN coatings after thermal shock by laser ablation

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The chemical composition and microstructural analyses on the surface of TiN coatings which were deposited onto SUS 304 substrates by an arc ion plating technique were investigated after heat-treatment using laser ablation. For a comparative study, as-deposited TiN specimens were heated at various temperatures for 30 minutes in a furnace. After the laser ablation, the surface of the TiN coatings exhibited cracks and spalling at the center of the ablated region and there was no noticeable phase variation including an increase of oxidized phases which were shown by the furnace heating process. The variation of binding energy peaks for the elements of TiN coatings showed that the laser thermal shock method reduced the effects of oxidation and impurities. The laser thermal shock method, consequently, could be subjected locally to thermo-mechanical stresses and enable a reduction of the side effects for a thermal shock test.

Key words: Thermal shock, Laser ablation, Oxidation effect, Surface crack, Thermo-mechanical stress.

Introduction

TiN hard coatings have been applied as a protective layer for hard metal tools, dies and many mechanical parts in order to enhance their lifetime and performance due to their remarkable physical and chemical properties such as high hardness, good wear resistance, and chemical stability [1, 2]. However, repeated thermal and mechanical loads can result in failures such as delamination, cracks or spalling in the interfacial region of the hard coatings, consequently, limiting tool lifetime. It is therefore important and useful to observe the thermal shock behavior on the surface of hard coatings.

For a given tool, the most important parameters which determine the amount of damage are the pulse maximum temperature and the thermo-mechanical stress in the coatings as a function of time [3]. Very high friction loads occur consistently between the tool and work piece with a millisecond range in a cutting process. In the industrial practice of machining the highest temperature up to 1000 °C will be applied to the tool surfaces [4], hence reducing the wear resistance as well as the thermo-mechanical properties of coatings.

In this study, the furnace heating method and the

laser thermal shock technique which have been studied widely for measuring the adhesive strength between substrate and coatings [5-7] were used to investigate the difference of the surface of TiN coatings. In the furnace heating process, the whole area of a specimen suffers from thermal shocks and is exposed to heat for a long time. By contrast, the laser thermal shock method can locally impacts the coating in a short time. Also, with the laser thermal shock method it is possible to apply thermal and mechanical impact on the coating, simultaneously, so it is similar to actual working conditions. This study was conducted to develop an understanding of the change in the microstructure and variation of the chemical composition of the TiN hard coatings after heat-treatment by a comparison of thermal shock methods.

Experimental Procedure

The titanium nitride (TiN) films were deposited onto SUS 304 substrates by an arc ion plating technique at 450 °C deposition temperature. The substrates were polished and cleaned with acetone and ethanol using ultrasonic cleaning. Before the TiN coatings were deposited, the substrates were sputter-cleaned using Ar ions under -800 V bias voltage for 10 minutes to remove the contaminant layer and to ensure good adhesion of the deposited coatings. The arc and sputter currents were maintained as 50A and 1.0A, respectively [8].

A high power Nd-YAG laser ablation system (LSX-

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213) was used to perform the thermal shock tests on the specimens. This system which is able to operate in a Q-switched mode was used to obtain 5 nanosecond pulses at a basic wavelength of 213 nm. The output of the laser power and spot sizes were adjusted by a computer-controlled system. Also, the spot has a homogeneous flat top energy profile and uniform density across all spot sizes. The specimen was repeatedly ablated by the pulsed laser on the same spot with 50% laser output and 200 μm spot sizes, and the number of laser ablation times increased from 1 to 15 while the beam duration time was fixed at 1 second. When delamination was observed in the surface of a TiN coating, the number of ablation times was determined as the critical point of coating failure. So a 7-times ablated specimen was chosen for a target observation which showed a specific delamination for the first time in this experiment. For a comparative study, four as-deposited specimens were heated at various temperatures from 500 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$ in the furnace and the heating time was fixed for 30 minutes.

After the heat-treatments, the surface morphologies of specimens were investigated by scanning electron microscopy (SEM, Hitachi S-4800) and the changes of crystal phase of the TiN coatings according to the source of the thermal loads were studied by means of X-ray diffraction (XRD, Bruker D8 Advance) analysis. The specimens were systematically analyzed by electron probe micro analysis (EPMA, CAMECA SX-100) and X-ray photoelectron spectroscopy (XPS, Thermo electron Co., ESCALAB 250) to observe the chemical composition and the atomic chemical state on the surface of the coatings.

Results and Discussion

Figure 1 shows the X-ray diffraction patterns for the specimens after the laser shock and the furnace heating at various temperatures from 500 to 800 $^{\circ}\text{C}$. High intensities of (111), (200), (220), and (222) diffraction peaks from the TiN coating layer and (111), (200) and (220) diffraction peaks from the SUS substrate were found on the as-deposited specimen [9]. The peak intensities of TiN decreased and those of FeNi increased with an increase of heating temperature up to 700 $^{\circ}\text{C}$. The preferred orientation of TiN coating can be explained by a competitive growth mechanism. The thermal energy from the furnace promotes the atomic rearrangement through diffusion and causes the growth of the (111) planes, so the (111) planes grow faster than the (200) planes [10]. When the temperature was increased to 800 $^{\circ}\text{C}$, the peaks from oxidized TiN coatings appeared and the peaks from the substrate were decreased. After laser ablation, the peak intensities of TiN decreased and those of FeNi increased slightly compared with the as-deposited specimen. But the XRD patterns of specimens after the

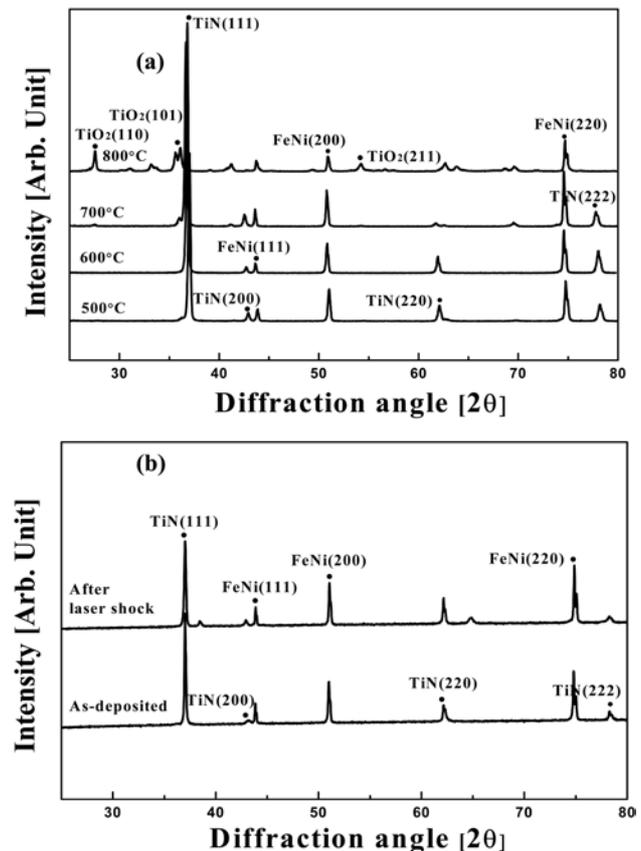


Fig. 1. XRD patterns of the TiN coating on SUS 304 substrates (a) after the furnace heating method at various temperatures and (b) after the laser shock method by a pulsed laser.

laser shock method showed similar patterns of as-deposited specimens without noticeable peak changes.

The surface morphologies of TiN coatings after the furnace heating processes are shown in Fig. 2. As-deposited films showed an irregular non-faceted spherical structure (Fig. 2(a)), but the structure changed to that with a pyramidal shape according to an increase in the temperature. After heating in the furnace at 500 $^{\circ}\text{C}$, the microstructure started to change to a faceted pyramidal structure (Fig. 2(b)) and at 600 $^{\circ}\text{C}$, the crystallites still revealed highly faceted structures (Fig. 2(c)). Also it was observed that the degree of crystallinity of films was affected by heat-treatment. Such a phenomenon might be related to the reduction of the residual stress during the furnace heating correlated with the relaxation of the strains by crystallization of the TiN crystals. During the furnace heating process, the compressive stress in the plane of the film decreased. This can be explained due to contraction in the substrate. In the case of a steel substrate, there is a compressive stress by a contribution to the film stress due to the difference of the thermal expansion coefficient of the film and substrate in cooling from the deposition temperature (673 K) to room temperature (293 K) [11].

Figure 3 shows the surfaces of ablated TiN coatings by the pulsed laser method. In Fig. 3(a)-(c), the color

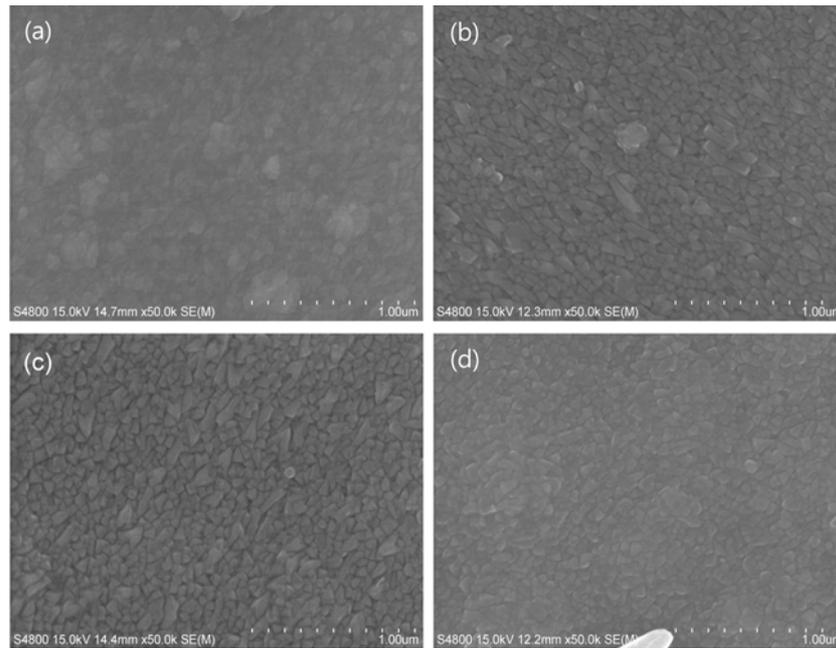


Fig. 2. Surface morphologies of TiN coatings after heat-treatment in the furnace (a) as-deposited, (b) 500 °C, (c) 600 °C, and (d) 700 °C.

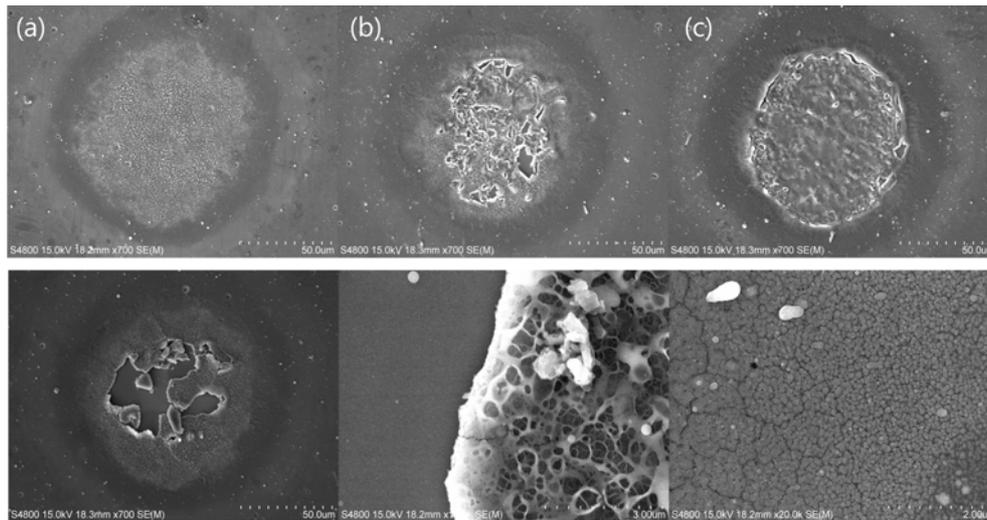


Fig. 3. Surface morphologies of TiN coatings after a number of laser ablation treatments (a) 4 times, (b) 10 times, (c) 15 times, (d) 7 times, (e) center of 7 times, and (f) boundary of 7 times.

Table 1. Chemical composition of TiN films measured by electron probe micro-analysis as a function of the heat-treatment method. (unit: at. %)

	Titanium (Ti)	Nitrogen (N)	Oxygen (O)
As-prepared	25.58	72.53	1.89
500 °C	26.25	53.70	20.05
600 °C	24.11	42.29	33.60
700 °C	25.80	28.68	45.52
After laser shock	24.56	72.93	2.50

and shape of the surface changed as a Gaussian distribution and the ablated spots gradually deteriorated

as the ablation time was increased. As shown in Fig. 3(d), observable spalling of a TiN coating by the laser ablation method started at the critical point (7 times). Fig. 3(e) shows that spalling of a TiN coating layer from the substrate occurred at the center of the spot, and the spread of cracks was diminished away from the center (Fig. 3(f)). At over the critical point (15 times), the TiN coating layer melted and re-adhered to the substrate because of the high energy density and continuous ablation by the pulsed laser (Fig. 3(c)).

It is observed that the surface morphologies of the TiN coatings were different according to the heat-treatments processes. The spalling and delamination of the coatings appeared on the surface of the ablated

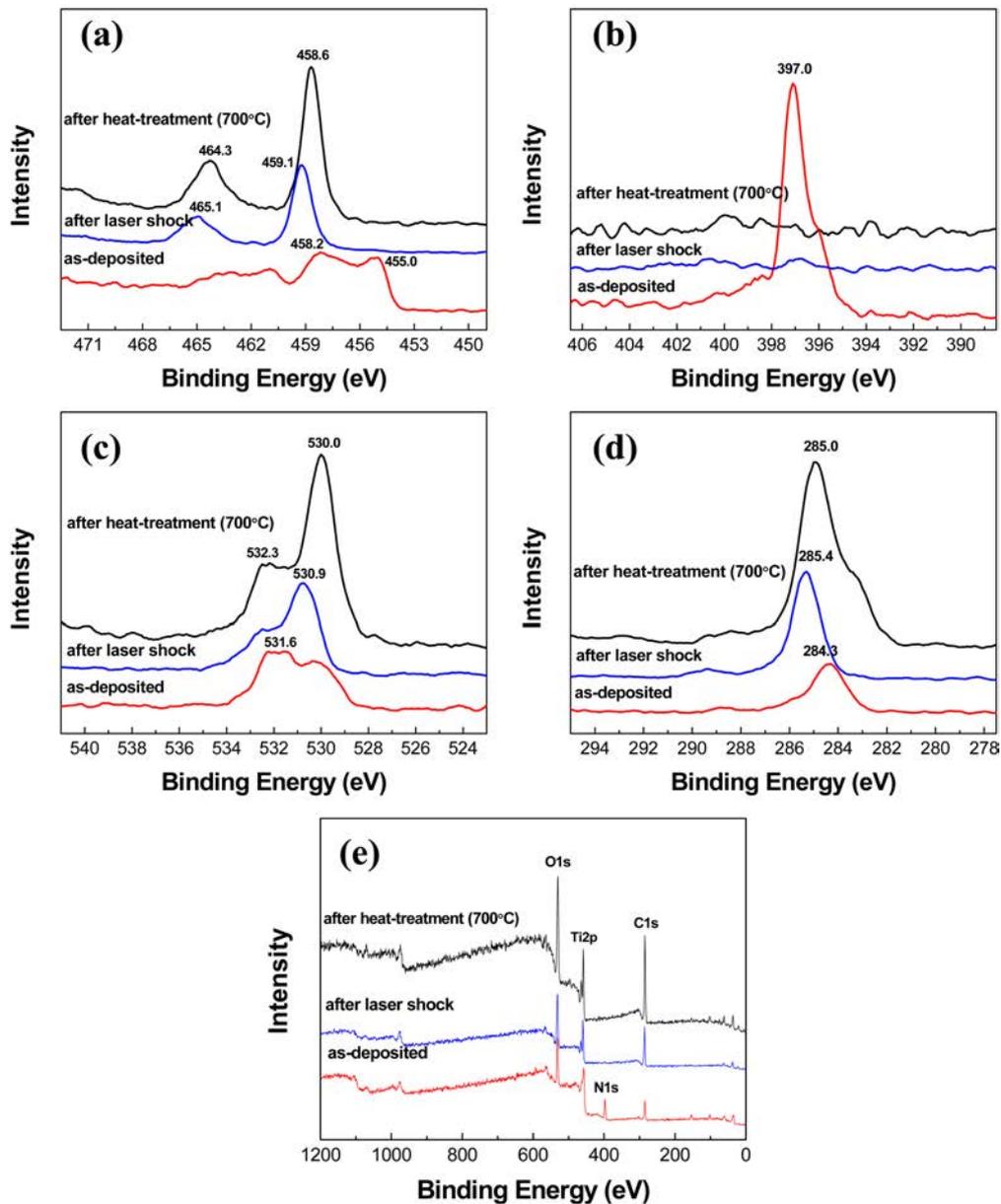


Fig. 4. The binding energies of TiN coatings (a) Ti2p XPS spectra, (b) N1s XPS spectra, (c) O1s XPS spectra, (d) C1s XPS spectra and (e) XPS wide scan spectra of each specimen.

specimens unlike the furnace heating process, so that these phenomena can indicate that the pulsed laser applied a thermal load and a mechanical load, simultaneously.

EPMA analysis was conducted to investigate the chemical compositions before and after heat-treatments of TiN coatings and the results are presented in table 1. These data were obtained as average values of 5 different points from the analysis. As seen in table 1, in the furnace heating process, a decrease of the nitrogen content and an increase of the oxygen content run linearly with an increase of the heat-treatment temperature and there was no observable change in the titanium content. This oxygen-rich phenomenon possibly originates from the oxidation when the specimens were heated in the furnace and cooled in ambient air [12]. After the laser

thermal shock process, the oxygen, titanium, and nitrogen contents of TiN film were approximately the same as their contents in the as-deposited specimen. In particular, the oxygen concentration of the coatings after laser ablation was significantly lower compared with specimens heat-treated in the furnace. It seems that there was an inadequate time for diffusion which takes place in the oxidation because the thermal loads caused by the laser ablation were rapidly applied and removed on the surface of the specimen.

Figure 4 shows the Ti 2p, N 1s, O 1s, and C 1s XPS spectra of the TiN films before and after the heat-treatments. The major peaks of the Ti 2p spectrum were 458.2 eV and 455 eV for the as-deposited specimen. Based on a comparison to the literature, the feature at

455 eV is assigned to TiN, and that at 458.2 eV to TiO₂ [13,14]. After heat-treatment at 700 °C in the furnace, the relative intensity of TiN was decreased while that of TiO₂ was increased with peak shifts to a higher binding energy. It is well known that as the oxidation temperature increases, Ti 2p_{3/2} peak shift to higher binding energy because the amount of the crystalline TiO₂ phase is increased [15]. After the laser thermal shock, the binding energy of the major peak has shifted to a slightly higher binding energy (459.1 eV) compared to the specimen heated in the furnace (458.6 eV). Also, the intensity of the major peak is lower than that of the heated specimen in the furnace. From Ti 2p spectrum data, it is deduced that the momentary temperature of the ablated spots was higher than 700 °C and a relatively thinner TiO₂ over-layer was formed on the surface of coatings.

The major nitrogen peak is centered at 397 eV and it can be attributed to titanium nitride [16]. Also there was no N 1s peak after the heat-treatments in the furnace and laser ablation because an oxide overlayer was formed on the surface of the coatings. Figure 4(c) and (d) show the O 1s and C 1s XPS spectra of TiN films, respectively. The O 1s spectrum before heat-treatments had a feature at 531.6 eV assigned to surface adsorbed oxygen [17]. After heating in the furnace, the major peak in the O 1s spectra was centered at 530 eV with a shoulder at 532.3 eV. The peak at 530 eV is related to oxygen chemically bound to Ti and the other peak at 532.3 eV was assigned to a C-O-type surface impurity [18]. In the C 1s spectra shown in Fig. 4(d), the peak at 284.3 eV of the as-deposited specimen was related to a C-C/C-H-type surface carbon impurity. After heating in the furnace, the major peak was located at 285 eV and it corresponds to a C-O-C-type carbon. The O 1s and C 1s spectra of the laser ablated specimen behaved almost in the same manner as those of the furnace heated specimen. However, the intensity of the laser ablated specimen was relatively lower. So, the pulsed laser ablation process could reduce the effect of impurities as well as the oxidation on the surface of TiN coatings as compared with the furnace heating process.

Conclusions

TiN coatings were prepared by an AIP technique onto SUS 304 substrates and then subjected to thermal shock by a laser ablation system. The furnace heating method was also used as a comparative study to investigate the difference of chemical compositions and microstructure on the surface of coatings. Crystalline TiN was changed from irregular non-faceted spherical crystals to a faceted-shape with an increase heating temperature in the furnace. After the laser thermal shock process, considerable surface cracks appeared on the coating. Through an analysis of chemical composition

on the surface of coatings before and after heat-treatments, the oxygen content of the TiN coating layer was significantly increased in the furnace heating process. The variation of binding energy peaks for the elements of TiN coatings is able to identify the decreased effects of oxidation and impurities during the laser method. From these results, it is confirmed that the application of pulsed laser to a thermal shock test can provide an effective test which is similar to the practical conditions of hard coating tools due to the loading of thermo-mechanical stresses.

Acknowledgement

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy (M-2009-01-0028), Republic of Korea, and partially supported by grants-in-aid for the NCRC (National Core Research Center) Program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (No. 2011-0006-257).

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