

Full Length Research Paper

Hardness-improvement of titanium using mixture gases

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Hardness of 99.7% titanium was improved in acetylene-ammonia mixtures at 1,250°C for 2 h. The flow rate of acetylene was set constantly at 0.4 cm³s⁻¹, but those of ammonia were varied over the range of 0 to 12 cm³s⁻¹. By using an X-ray diffractometer (XRD) and an energy dispersive X-ray (EDX) analyzer, TiC, TiN, TiC_{0.7}N_{0.3}, and TiC_{0.3}N_{0.7} phases with the corresponding elements were detected. Knoop hardness (HK) of the sample was at the highest when it was processed in only acetylene. Their hardness values were decreased, but their surfaces became rougher, due to the increase of ammonia flow rates.

Key words: TiC, TiN, TiC_{0.7}N_{0.3}, TiC_{0.3}N_{0.7}, Knoop hardness.

INTRODUCTION

Titanium and its alloys are now vastly expanding into many field, such as aeronautical and chemical industries, marine, power generation, sports and leisure transportation, and biomedical devices, due to their high strength and excellent corrosion resistance, low density, high strength-to-weight ratio, low modulus and good biocompatibility. However, titanium and its alloys with low hardness usually have poor wear resistance and high friction coefficient, which limits their application in engineering (Guo et al., 2011). Some titanium implants are intended for long term or permanent location, for example, as orthopaedic joint prostheses. A clinical problem sometimes encountered with titanium implants and their abutments is that they are relatively soft and easy to damage. The addition of thin hard coating to the surface of titanium might overcome those problems, that is. to protect titanium against oxidation and to improve surface hardness. Therefore, continuous research had been directed towards surface modification of titanium (Ferro et al., 2008). Research in the field of advanced ceramics had focused on the exploration of new routes to produce non-oxide materials, such as carbides, nitrides, borides, and sulfides (Aghababazadeh et al., 2007).

Among transition metals, titanium carbide, and nitride may be used for improving the poor surface properties

due to their high hardness, wear resistance and chemical inertness (Leparoux et al., 2008). In addition, titanium carbonitride have been successfully introduced in the metal cutting industry (Jun et al., 2009). Surface coatings of titanium nitride, carbide, and carbonitride can be made by chemical vapor deposition (CVD), physical vapor deposition (PVD), anodizing, plasma and laser nitriding, and thermal oxidation and ion implantation (Jin et al., 2009). The CVD and PVD of titanium are rather expensive. They need high vacuum systems and toxic chemicals. Titanium carbide, nitride, and carbonitride can be formed by direct metal-gas reaction which is an inexpensive and non-toxic process. The purpose of the present research is to improve hardness of titanium using the simple process which is benign to environment. It can be done on a large scale as well.

MATERIALS AND METHODS

Samples were prepared from titanium rod (99.7%) with the impurities as follows: Fe: 0.05 at%, C: 0.05 at%, N: 0.05 at%, O: 0.05 at%, and H: 0.015 at%. The rod was cut into the disks with about 20 mm diameter and 1 to 2 mm thick. The disks were ground with silicon carbide (SiC) papers and polish with 0.3 μm alumina powder, and then they were cleaned with alcohol. Each of them was put in a high temperature reaction chamber made of quartz as shown in Figure 1. The air was removed by evacuation to 17.33 kPa absolute pressure, and purified argon was slowly fed into the chamber. The process was repeated ten times. The residual content of oxygen in the chamber before starting the reaction was

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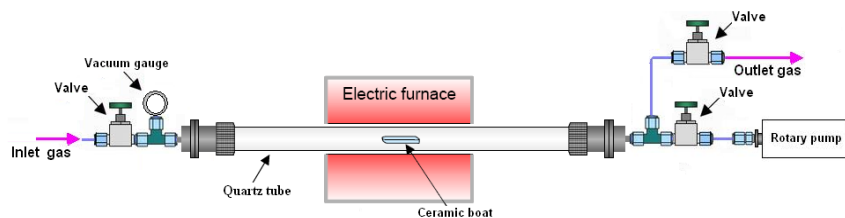


Figure 1. High temperature reaction chamber.

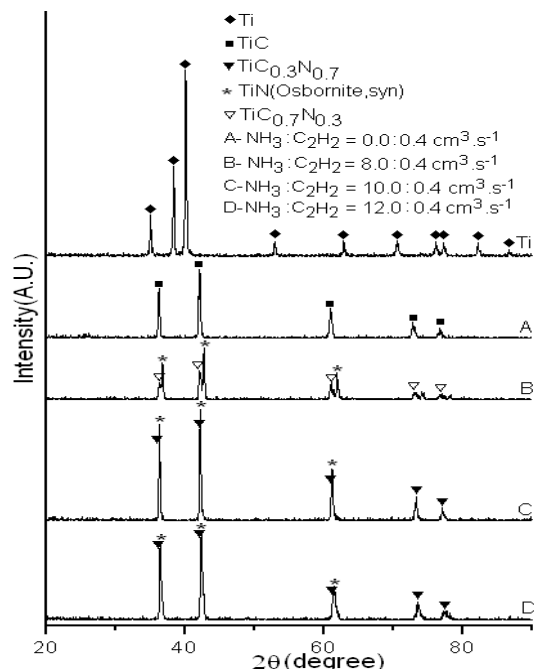


Figure 2. XRD spectra of Ti before and after processing at 1,250°C for 2 h.

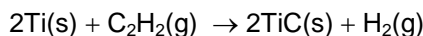
calculated using the equation of state of an ideal gas and 20 volume % O_2 in ambient atmosphere, and it was found to be not more than 5 ppb. Each of the samples were heated in $10 \text{ cm}^3 \text{ s}^{-1}$ argon until the test temperature was obtained. Then $0.4 \text{ cm}^3 \text{ s}^{-1}$ acetylene and 0, 8, 10 and $12 \text{ cm}^3 \text{ s}^{-1}$ ammonia were fed into the chamber. The process proceeded at $1,250^\circ\text{C}$ for 2 h. At the end of the process, the furnace, ammonia, and acetylene were turned off. The samples were cooled down to room temperature and brought for further analysis. The samples were measured ten times using 5 s dwelling time and 50 gf load for a Knoop micro-hardness tester (MXT- α 7 Matsuzawa Seiki), X-ray diffractometer [(XRD) XRD BRUKER AXS company series D8 ADVANCE] in combination with JCPDS software (Powder Diffraction File, 2001), and SEM equipped with EDX (Jeol : JSM-6335F).

RESULTS AND DISCUSSION

X-ray diffraction

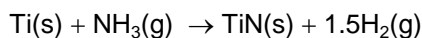
XRD patterns in Figure 2 showed the detection phases of

Ti, TiC, TiN, $TiC_{0.7}N_{0.3}$, and $TiC_{0.3}N_{0.7}$. Before processing, only Ti was detected (JCPDS number 44-1294). TiC, TiN, $TiC_{0.7}N_{0.3}$, and $TiC_{0.3}N_{0.7}$ were produced in the mixture of acetylene and ammonia gases at $1,250^\circ\text{C}$ for 2 h. At $NH_3:C_2H_2 = 0:0.4$, only TiC phase was detected (JCPDS number 02-1179). At $NH_3:C_2H_2 = 8:0.4$, TiN and $TiC_{0.7}N_{0.3}$ phases were detected (JCPDS numbers 06-0642 for TiN, and 42-1489 for $TiC_{0.7}N_{0.3}$) (Zhou et al., 2009). When NH_3 flow rates were increased to 10 and $12 \text{ cm}^3 \text{ s}^{-1}$, TiN and $TiC_{0.3}N_{0.7}$ phases were detected (JCPDS number 42-1488 for $TiC_{0.3}N_{0.7}$) (Xiang et al., 2009). At $NH_3:C_2H_2 = 0:0.4$, Ti reacted with C_2H_2 to form TiC by the reaction:



TiC(s) deposited on the titanium surfaces, and $H_2(g)$ and residual of $C_2H_2(g)$ were drained off into the ambient atmosphere (Sopunna et al., 2004).

At $NH_3:C_2H_2 = 8:0.4$, NH_3 was added to the C_2H_2 gas system, NH_3 and C_2H_2 reacted with Ti to form nitride and carbonitride phases as explained below. At a temperature of $1,250^\circ\text{C}$, TiN ($\Delta G_{TiN} = -195 \text{ kJ.mol}^{-1}$) is a little more thermodynamically stable than TiC ($\Delta G_{TiC} = -167 \text{ kJ.mol}^{-1}$) (Wicks and Block, 1963). At this stage, Ti reacted with NH_3 to produce TiN (Sopunna et al., 2006) by the reaction:



Due to the equilibrium of Ti, NH_3 , and C_2H_2 , $TiC_{0.7}N_{0.3}$ was produced and detected as well. In the same case, at $NH_3:C_2H_2 = 10$ and $12:0.4$, NH_3 was added to increase the ratio of N atom more than that of the C atom.

Knoop hardness (HK)

HK average value was calculated and shown in Figure 3. HK value of the substrate before processing was $136.8 \pm 12.4 \text{ kgf.mm}^{-2}$. For the present research, HK was successfully improved by the carburization and carbonitridation. It was decreased with the increase in the NH_3 flow rates. At $NH_3:C_2H_2 = 0:0.4$, HK value of the sample was at maximum at $465.0 \pm 33.2 \text{ kgf.mm}^{-2}$ (3.4 times of the substrate), due to TiC formation on its surface. This shows that TiC played the role in improving

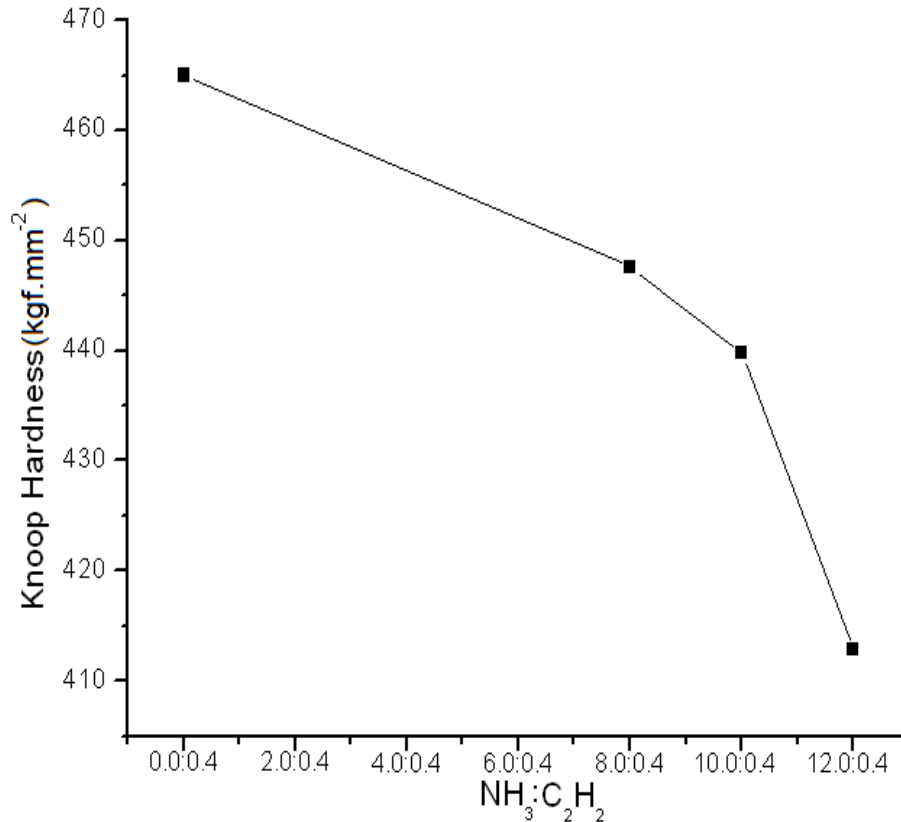


Figure 3. KH of titanium at different flow rate ratios of NH₃ to C₂H₂.

hardness of the substrate (Zhang et al., 2006).

When NH₃ flow rates was added and gradually increased from 0 to 12 cm³s⁻¹, HK values were parabolically decreased with an increase in the NH₃ flow rates. It shows that hardness of the samples was controlled by the formation of new phases deposited on the substrates. Therefore, HK values were controlled by the flow rate of NH₃ gas, which led to different deposited phases on the substrates (Rebelo de Figueiredo et al., 2008).

Energy dispersive x-ray (EDX)

By using EDX, elemental spectra of the samples before and after processing at 1,250°C for 2 h are shown in Figure 4. Before processing, only Ti was detected. After processing in C₂H₂, Ti, and C were detected (Liu et al., 2008). When N was added to the system, additional N was detected (Yang et al., 2008). H is a light element; therefore, it was not detected.

Scanning electron microscope (SEM)

SEM micrographs for as received titanium and the

titanium coated at 1,250°C for 2 h are shown in Figures 5a to e. The micrographs shows the difference between a plain surface of as received and a rough surface of the titanium coated at 1,250°C for 2 h resulting from the formation of the new phase, which could be TiN, TiC, TiC_{0.7}N_{0.3}, and TiC_{0.3}N_{0.7}. The layers are irregular showing that the reactive gases reacted with titanium. The reaction leads to surface roughness which reflects their tribological properties. It is worth noting that surface roughness was increased with the increase in the ammonia flow rates. At this stage, more products were deposited on the substrates.

Conclusions

Hardness of Ti was successfully improved by the 1,250°C processing in acetylene and ammonia mixtures ranging from NH₃:C₂H₂ ratios of 0:0.4 to 12:0.4 for 2 h. The maximum HK value of the sample was 3.4 times of the substrate, when it was processed in 0.4 cm³s⁻¹ C₂H₂. HK values were decreased with the increase of ammonia flow rates. It was caused by the formation of carbonitrides analyzed using XRD and EDX. SEM micrographs showed that their surfaces were covered with the deposited phases of nitride, carbide, and carbonitrides

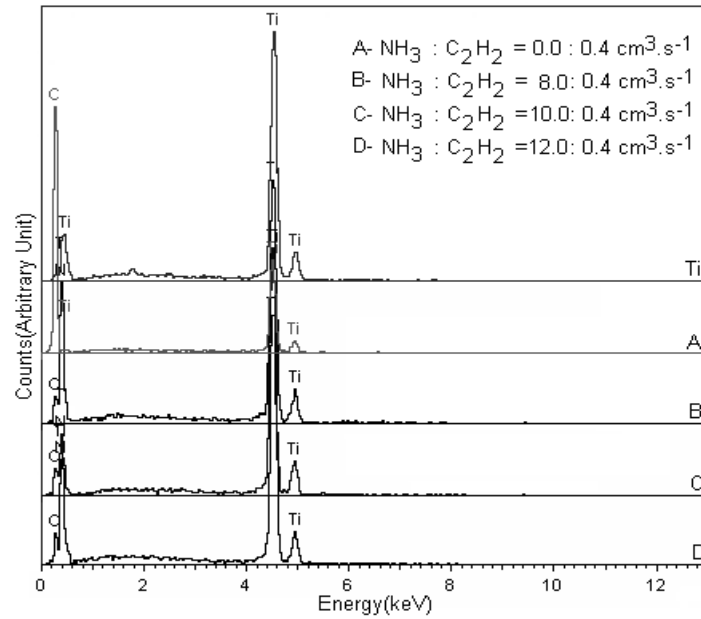


Figure 4. EDX spectra of as-received Ti and Ti with 1,250°C and 2 h processing in NH₃:C₂H₂ ratios of 0:0.4, 8:0.4, 10:0.4, and 12:0.4, respectively.

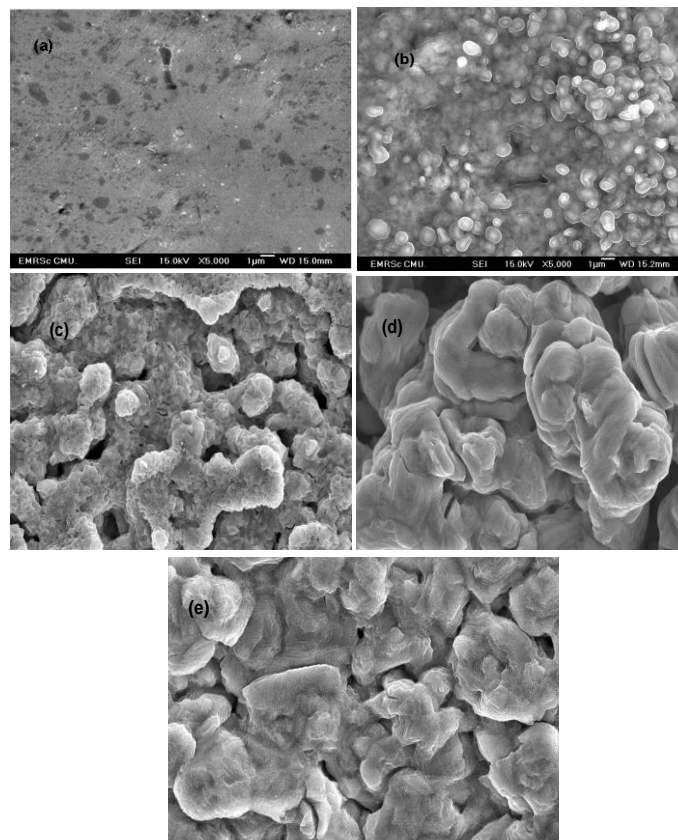


Figure 5. SEM micrographs of a) as received Ti, and b) to e) Ti with 1,250°C and 2 h processing in NH₃:C₂H₂ ratios of 0:0.4, 8:0.4, 10:0.4, and 12:0.4, respectively.

reflecting the surface properties.

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