

An XPS study of titanium-chromium nitride (Ti,Cr)N nanopowder prepared by heat treatment in flowing nitrogen gas

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The electrical wire explosion of Cr-coated Ti wires produced nanosized particles consisting of various phases such as β (Ti,Cr), α -Ti, TiCr₂, and TiN. The particles were heat treated at 800 °C ~ 1100 °C in flowing N₂ gas in an effort to synthesize a ternary nitride, (Ti,Cr)N. An X-ray diffraction study revealed that they transformed to a single-phase (Ti,Cr)N during heating at 1100 °C for 1 h. An X-ray photoelectron spectroscopy (XPS) was used to examine the electronic configurations of Ti, Cr, and O after nitriding at various temperatures. After heating at 800 °C, the metallic Cr 2p peak vanished in accord with the disappearance of the β (Ti,Cr) phase confirmed by XRD. The inspection of XPS spectra suggested that the electronic configuration of (Ti,Cr)N is identical to that of TiN. The metal to nitrogen ((Ti + Cr) / N) ratio decreased with the nitriding temperature becoming 1 after heating at 1100 °C. XPS quantification revealed that the ternary nitride had the composition of (Ti_{0.6}Cr_{0.4})N.

Key words: TiN, CrN, (Ti,Cr)N, Wire explosion, XPS.

Introduction

Titanium and chromium nitrides have been widely applied as important materials in industrial, technological, and scientific areas because of their excellent properties (e.g., hardness, low friction, or wear resistance). A TiN thin film is liable to oxidation at high temperatures above 500 °C, forming TiO₂ at the surface [1]. A CrN coating shows higher oxidation resistance at a maximum temperature of 750 °C [2]. In order to further improve their properties, many studies including ternary nanocomposites such as (Ti,Al)N or (Ti,Cr)N have been conducted [3-5].

Chromium is well known to form a solid solution with titanium. Although ternary (Ti,Cr)N thin films of various compositions have been reported to enhance the thermal stability, [4-6] it is still at an early stage in comparison to binary nitride films. Furthermore, very limited attention has been paid to the synthesis or characterization of bulk (Ti,Cr)N nanopowder [7,8].

We recently synthesized TiN and (Ti,Cr)N nanoparticles using the electrical wire explosion (EWE) method and examined them with X-ray diffraction (XRD) and field-emission transmission electron microscopy (FE-TEM) [7]. In this study, we carried out an XPS study to further characterize (Ti,Cr)N nanoparticles prepared at different

nitriding temperatures, focusing on a change of the chemical environment for Ti, Cr, N, and O atoms on the surface.

Experimental Procedure

The preparation method of Ti-Cr, TiN, and (Ti,Cr)N nanoparticles is described in more detail in our previous papers [7,9]. The explosion of Cr-coated Ti wire in Ar produced nano-sized powders of various phases such as β (Ti,Cr), TiCr₂, α -Ti and TiN. To synthesize a ternary nitride, the powders were heated in a tube furnace for 1 h at 800 °C, 900 °C, 1000 °C, and 1100 °C in flowing N₂ gas. TiN nanopowders were used for a comparison purpose which were previously synthesized in our laboratory using the electrical explosion of Ti wire in N₂ gas [10]. After heat treatment, they were examined by XPS using a VG Scientific ESCALAB250 XPS system (UK) equipped with a monochromated Al K α X-ray source ($h\nu = 1486.6$ eV) with charge compensation at the Busan center of Korea Basic Science Institute (KBSI). The spot diameter was 500 μ m and the emitted photoelectrons were detected by a multichannel detector at a takeoff angle of 90° relative to the sample surface. The base pressure was 1×10^{-9} Pa (0.1×10^{-12} bar). Initial survey spectra were obtained with a 1.0 eV step size in the CAE (constant analyzer energy) mode of 50 eV. High-resolution spectra for Ti 2p, Cr 2p, N 1s, and O 1s were acquired with a 0.10 eV step size in the CAE mode of 20 eV. All of the binding

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energies (BEs) obtained were compensated by the hydrocarbon C1s peak at 284.6 eV. Synthesized TiN [10] nanopowder was used as the reference material. Pristine powder samples including oxidized surfaces were used in the XPS analysis because sputtering is impractical to apply to powder samples for XPS analysis. Quantitative peak analysis was performed using the Shirley's background subtraction method.

Results and Discussion

The wire explosion of Cr-coated Ti wire produced various phases such as $\beta(\text{Ti,Cr})$, TiCr_2 , $\alpha\text{-Ti}$ and TiN. Table 1 lists the phases identified by X-ray diffraction after heat treatment at various temperatures. Here, and represent the relative amounts of each phase in descending order. The most significant observation is that the meta-stable $\beta(\text{Ti,Cr})$ phase decomposed completely on nitriding at 800 °C. Accordingly, $\alpha\text{-Ti}$ increased at the expense of $\beta(\text{Ti,Cr})$ and Ti_2N phases was newly produced on heating. The Ti_2N phase was stable up to 1000 °C and disappeared at 1100 °C. In the end, a single-phase $(\text{Ti,Cr})\text{N}$ was synthesized during the heat treatment at 1100 °C.

The Ti 2p XPS photoelectron lines of the as-exploded and as-nitrided nanopowders are shown in Fig. 1. The most intense peak from all samples was located at around 458.0 eV and was attributed to titanium oxides (Ti_xO) [11,12]. As the nitriding temperature increased complex-shaped peaks developed between 454.7 to 456.5 eV which implies a modification of the electronic structure of Ti atoms. The complex Ti 2p XPS photoelectron lines have often been explained in terms of the energy loss peaks, which are typical for Ti 2p peaks of TiN-related compounds such as TiN and $(\text{Ti,Al})\text{N}$ [12-14]. The splitting of the peak for individual species (i.e., titanium oxides, nitride, oxynitrides, their energy loss) is quite complicated and beyond the scope of this study. It is, however, noteworthy that the chemical environment of Ti in nitrided products is altered towards that of TiN as the heating temperature increases. Thereby, $(\text{Ti,Cr})\text{N}$ synthesized at 1100 °C provides an electronically identical environment for Ti atoms to the TiN compound in view of the Ti 2p XPS spectra. This agrees with similar work by Strydom and

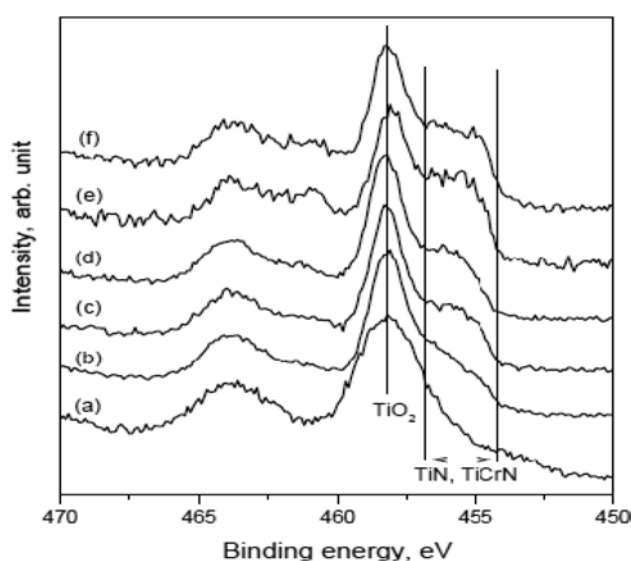


Fig. 1. Ti 2p XPS photoelectron lines of the explosion products in Ar of Cr-coated Ti wire and after heat treatment in N₂ at various temperatures. (a) as-exploded (b) after nitriding at 800 °C (c) after nitriding at 900 °C (d) after nitriding at 1000 °C (e) after nitriding at 1100 °C (f) TiN nanopowder prepared by wire explosion of Ti wire in N₂ gas.

Hofmann, [14] where they found that the binding energies of Ti 2p photoelectron peaks of $(\text{Ti,Al})\text{N}$ were indistinguishable from those of TiN. From the above results, it is apparent that the complex-shaped peaks represent the $(\text{Ti,Cr})\text{N}$ phase. $(\text{Ti,Cr})\text{N}$ is likely to be produced by the substitution of Cr for Ti in the TiN structure without a noticeable structural distortion, although the kinetics and mechanism of Cr diffusion into TiN structures for solid-solution formation is still obscure.

The peak positions of the Cr 2p XPS spectra contain important information on the electronic environment of the Cr-N compound. The incorporation of N into Cr-N or Ti into $(\text{Ti,Cr})\text{N}$ is known to the electronic environment of the Cr 2p spectra. It is documented that the peak position of Cr in Cr-N compound shifts towards higher energy with regard to metallic Cr due to the incorporation of more electronegative N [15]. On the other hand, the binding energy of Cr in $(\text{Ti,Cr})\text{N}$ is known to be lower than that in Cr-N [6].

The Cr 2p XPS peaks are depicted in Fig. 2. They contain a broad peak of chromium oxides (the peak position at ~ 575.5 eV) owing to the oxidized surface [17]. This makes the distinction of specific Cr species difficult. Nevertheless, two distinctive features are noted in Cr 2p XPS peaks. One is the discernible metallic Cr peak (~573.0 eV) [17] in the as-exploded sample which vanished after nitriding at 800 °C. This suggests that metallic Cr has almost completely reacted with N during heat treatment at 800 °C. The other is the shift of the Cr peak towards the lower energy side at higher nitriding temperatures. As previously stated, the binding energy of Cr is expected to depend on the

Table 1. Phases in as-exploded and as-nitrided nanopowders identified by X-ray diffraction.

Sample	$\beta(\text{Ti,Cr})$	$\alpha\text{-Ti}$	Ti_2N	TiCr_2	TiN	$(\text{Ti,Cr})\text{N}$
As exploded	⊙	△	-	⊙	△	-
800 °C	-	⊙	○	○	○	-
900 °C	-	○	○	-	○	○
1000 °C	-	△	○	-	-	○
1100 °C	-	-	-	-	-	⊙

⊙ major ○ medium ⊙ minor

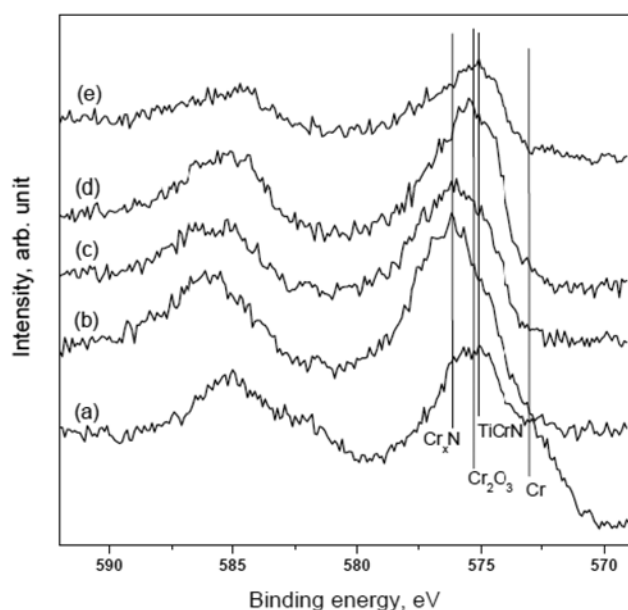


Fig. 2. Cr 2p XPS photoelectron lines of the explosion products in Ar of Cr-coated Ti wire and after heat treatment in N_2 at various temperatures. (a) as-exploded (b) after nitriding at 800 °C (c) after nitriding at 900 °C (d) after nitriding at 1000 °C (e) after nitriding at 1100 °C.

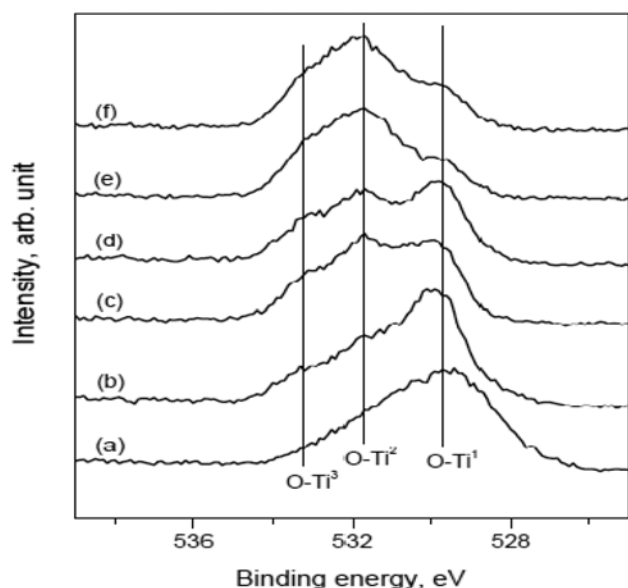


Fig. 3. O 1s XPS photoelectron lines of the explosion products in Ar of Cr-coated Ti wire and after heat treatment in N_2 at various temperatures. (a) as-exploded (b) after nitriding at 800 °C (c) after nitriding at 900 °C (d) after nitriding at 1000 °C (e) after nitriding at 1100 °C (f) TiN nanopowder prepared by wire explosion of Ti wire in N_2 gas

relative amounts of Cr-N and (Ti,Cr)N phases. X-ray diffraction data showed that the (Ti,Cr)N phase increased with the nitriding temperature (Table 1). Therefore, it can be assumed that the peak shift towards the lower energy side is related to the increase in the amount of the (Ti,Cr)N phase. The Cr 2p peak from the sample nitrided at 1100 °C has a maximum position at 575.0 eV which agrees with a previous result of

Table 2. Metal-to-nitrogen ratio of explosion products after heating at various temperatures in flow N_2 gas.

Temperature	Ti/N	Cr/N	(Ti+Cr)/N
800 °C	1.2	0.6	1.8
900 °C	0.9	0.5	1.4
1000 °C	0.8	0.5	1.3
1100 °C	0.6	0.4	1.0

synthesized (Ti,Cr)N [16].

The O 1s spectra of (Ti,Cr)N synthesized at 1100 °C (e) was very close to that reported for TiN [13] and also to that of TiN nanopowders (f) we synthesized previously. The O species at the near-surface area range from oxides or oxyhydroxides of all contained elements even to bonded water at the surface. As a result, it is often difficult to monitor and interpret the chemical environment of O species by the XPS technique. Nevertheless, the O 1s XPS spectra of our samples exhibited discernable peaks at 529.7, 531.7, and 533.1 eV. Fig. 3 shows the O 1s XPS photoelectron lines of nitrided samples. The binding energies match completely with the results of Jouan et al. [13] who reported three peaks at 529.8 eV, 531.3 eV and 533.1 eV in O 1s XPS spectra of TiN. Obviously, it is apparent that the electronic environment of O species at the near-surface of (Ti,Cr)N is comparable to that of TiN.

XPS quantification has been used to determine the relative concentrations of each element. Table 2 lists the relative atomic concentrations in samples after various heat treatments. The metal-to-nitrogen ((Ti + Cr)/N) ratio was measured as the area ratio between the N 1s and the entire region of the Ti 2p and Cr 2p signal. This allows the determination of the metal-to-nitrogen ratio irrespective of how Ti and Cr are chemically bonded. It is seen that the metal-to-nitrogen ratio ((Ti + Cr)/N) decreases with the nitriding temperature. This can be explained by the attenuation of low-N phases such as α -Ti, $TiCr_2$ and Ti_2N as can be noticed in Table 1. It eventually converges to a stoichiometric nitride at 1100 °C giving the composition of $(Ti_{0.6}Cr_{0.4})N$. In summary, this study demonstrated that (Ti,Cr)N synthesized by heat treatment has an identical electronic configuration to TiN under the resolution of XPS.

Conclusions

An XPS investigation was performed to characterize (Ti,Cr)N nanoparticles prepared by nitriding the explosion products of Cr-coated Ti wire in flowing N_2 gas at different temperatures (800 °C, 900 °C, 1000 °C, or 1100 °C). The synthesis of ternary (Ti,Cr)N nanopowders was achieved at 1100 °C. The results are as follows:

(1) The metal-to-nitrogen ratio ((Ti + Cr)/N) of nitrided products decreased with the nitriding temperature due to the attenuation of low-N phases such as $TiCr_2$, α -Ti and Ti_2N on heating. (Ti,Cr)N synthesized at 1100 °C had a stoichiometric ratio of 1 having the composition of

(Ti_{0.6}Cr_{0.4})N.

(2) Ti 2p XPS spectra revealed the most pronounced peak of titanium oxides (Ti_x-O) at around 458.0 eV. As the reaction temperature increased, (Ti,Cr)N peaks emerged between 454.7 to 456.5 eV converging to the TiN structure.

(3) The metallic Cr peak at 573.0 eV vanished after nitriding at and above 800 °C. The Cr 2p peak shifted towards the lower energy side with the evolution of the (Ti,Cr)N phase. The Cr 2p peak of (Ti,Cr)N synthesized at 1100 °C showed a binding energy at 575.0 eV. O 1s XPS spectra of the samples exhibit discernable peaks at 529.7, 531.7, and 533.1 eV.

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