Electrical Wire Explosion of Cr-Coated Ti Wire in N₂ Gas

Wonbaek Kim¹, Sujeong Lee^{1,*}, Chang-yul Suh¹, Sung-wook Cho¹,
Taegong Ryu¹, Je-shin Park² and In-Jin Shon²

¹Mineral Resource Research Division, Korea Institute of Geoscience and Mineral Resources,
92 Gwahang-no, Yuseong-gu, Daejeon 305-350, Korea

²Division of Advanced Materials Engineering, Chonbuk National University, Chonbuk 561-756, Korea

Cr-coated Ti wire was electrically exploded in N₂ gas. The diameter of Ti wire was 0.289 mm and the thickness of Cr coating was 0.033 mm, which corresponds to the average composition of about 25 at% Cr. X-ray diffraction and FE-TEM study revealed that the explosion products consisted of cube-shaped TiN, sphere-shaped Cr₂N, and clusters of extremely fine particles. The average particle size of TiN and Cr₂N was about 35 and 38 nanometers, respectively. The size of the fine particles was small as a few nanometers and clustered heavily. Therefore, it was not possible to examine individually. The particles contained about 28 at% Cr. In some part of the high resolution TEM image, cubic structure could be recognized. The lattice parameter of the particles calculated assuming cubic structure was smaller than TiN and larger than CrN. As a result, it was concluded that the fine particles are (Ti,Cr)N. [doi:10.2320/matertrans.M2010205]

(Received June 11, 2010; Accepted August 6, 2010; Published October 14, 2010)

Keywords: wire explosion, titanium nitride, Cr₂N, (titanium,chromium)N, nanoparticle

1. Introduction

Titanium nitride (TiN) has been studied extensively due to its excellent physical and chemical properties. The particulate form of TiN was prepared by various methods. Self-propagating high-temperature synthesis (SHS) was used frequently to produce TiN powders.¹⁻⁴⁾ Nanosized TiN particles were produced by carbothermally reducing titanium oxides in N₂ atmosphere.⁵⁾ It was also synthesized by vapor-phase reaction of titanium tetrachloride in N₂ or ammonia gases.⁶⁻⁸⁾ More recently, we also reported a successful synthesis of TiN nanoparticles by exploding Ti wire in N₂ gas.⁹⁾

Similarly, (Ti,Cr)N has been studied recently in an effort to modify TiN and been prepared as thin film as a rule.¹⁰⁻²³⁾ However, no efforts have been devoted to synthesize (Ti,Cr)N as particulate form. The only study on this subject was conducted using a rather complicated precipitation method in which Cr₂O₃ and TiO₂ nanocomposite powder were utilized.²⁴⁾

We have been demonstrated that electrical wire explosion (EWE) would be a plausible method to synthesize various alloys and intermetallic nanoparticles²⁵⁻²⁸⁾ and also nitride.²⁹⁾ In this study, we elaborated further to synthesize (Ti,Cr)N nanoparticles by this method.

2. Experimental Procedure

The Ti-Cr wire for EWE was prepared by the electro-deposition of Cr on ϕ 0.289 mm Ti wire. The detailed procedure for the continuous electrodeposition set-up is described in our previous papers.^{25,26)} The diameter of the Cr-coated Ti wire was 0.320 mm which gives the average composition of about 25 at% Cr. The Cr-plating solution consisted of 2.47 mol/L of chromic trioxide and 0.03 mol/L of sulfuric acid. The temperature for the deposition was maintained at 40°C. The Cr-coated Ti wire was then loaded

to the chamber for explosion experiments. Explosion of Ti wire was conducted in a 30-liter airtight chamber. The chamber was evacuated preliminarily and filled with pure nitrogen gas at the chosen pressure. The wire was exploded under the nitrogen pressure of 0.1013 MPa. The capacitance of the exploding circuit was 3.5 μ F. The applied voltage across the 20 mm-long wire was 11.4 kV. The total number of explosion for each condition was about 600. After the explosion, the powders were stabilized overnight and filtered through a 125 μ m sieve to remove some misfired portions. The particles were then examined by Field-Emission Transmission Electron Microscopy at KBSI (FE-TEM, JEM 2100F, Jeol Ltd., Japan), and X-ray Diffraction (XRD, D/MAX 2200, Rigaku Corp., Japan) with Cu K α radiation.

3. Results and Discussion

Previously, we reported the successful synthesis of single-phase TiN nanoparticles by EWE of pure Ti wire in N₂ gas.²⁹⁾ We also conducted explosion experiments in Ar gas using the Cr-coated Ti wire which is the same as the one used in this study.²⁸⁾ We produced α -Ti and TiCr₂ nanoparticles which are the equilibrium phases of Ti-Cr alloy of the corresponding composition. However, neither of the phases was identified in this study when it was exploded in N₂ gas.

From the morphological point of view, the explosion products of this study can be classified into three categories. The 1st case was cube-shaped TiN. The 2nd was sphere-shaped Cr₂N. The 3rd was clustered particles of a few nanometers in size. Both TiN and Cr₂N allowed straightforward identification by either selected area electron diffraction (SAED) patterns or diffractograms. However, the fine 3rd particles were difficult to be examined individually even under our high-resolution TEM due to their fine size and clustering tendency.

Figure 1 shows the diffraction pattern of the explosion products. The pattern was indexed to cubic TiN (JCPDS 38-1420) and hexagonal Cr₂N (JCPDS 35-0803) as marked on the pattern. At a glance, it appeared to be a single phase TiN

*Corresponding author, E-mail: crystal2@kigam.re.kr

Fig. 1 X-ray diffraction pattern of nanoparticles produced by electrical explosion of Cr-coated Ti wire under 0.1013 MPa N_2 gas.

owing to the weak Cr_2N peaks because the main peak of $Cr_2N(111)$ overlaps with that of $TiN(200)$ and, what is more, the 2nd strongest peak of $Cr_2N(002)$ is only 21% of the main peak. The lattice parameter of the TiN phase was calculated to be 0.42304 nm, which is slightly less than that of 0.42417 nm (TiN , JCPDS 38-1420).

The free energy of formation of Cr_2N is lower than that of CrN . CrN is known to convert to Cr_2N at temperatures above $1000^\circ C$.³⁰⁾ Considering the thermodynamic stability of TiN and Cr_2N phases, it appears to be reasonable that CrN phase was not observed in this study. This agrees with the result of A. Matsunawa and S. Katayama.³¹⁾ They reported that only Cr_2N was synthesized by the laser ablation of pure Cr target in N_2 gas.

TiN and Cr_2N phases were confirmed by TEM analysis. Figure 2 shows the TEM image (a) and corresponding diffractogram (b) of a cube-shaped particle. The diffractogram reveals that it has the cubic structure. The lattice parameter a was calculated to be 0.4224~0.4242 nm. The shape of TiN particle was exactly the same as we previously obtained by exploding pure Ti wire in N_2 gas.²⁹⁾

Figure 3 shows the TEM image (a) and corresponding diffractogram (b) of a round-shape particle. The diffractogram was obtained by fast Fourier transformation and indexed to hexagonal $\beta-Cr_2N$ (JCPDS 35-0803). The average particle size of TiN and Cr_2N was about 35 nm and 38 nm, respectively. However, it should be noted here that we did not perform an extensive study to determine the particle size and distribution statistically since it was not the main subject of our study.

Now returning to our attention to 3rd particles, our FE-TEM study was rather limited due to their fine size and clustering tendency. Nevertheless, efforts to elucidate the nature of the particles were made through careful study on high resolution images and diffractograms. Figure 4 shows the TEM micrograph (a), corresponding diffractogram (c), and higher-resolution TEM micrograph (b). As can be seen in this figure, the size of the particles is only a few nanometers. The diffractogram on the left inset of Fig. 4(b) shows that the corresponding center region of the sample holds the cubic symmetry. The lattice parameter of the particles was calculated from the ring patterns of the diffractogram shown on Fig. 4(c) assuming a cubic structure. The lattice parameter obtained thereby was 0.4206 nm, which is smaller than 0.42417 nm (TiN , JCPDS 38-1420) and larger than 0.4139 nm (CrN , JCPDS 11-0065). Therefore, it appears that the fine particles could be $(Ti,Cr)N$.

Figure 5 shows the scanning transmission electron microscope (STEM) image and EDS spectrum of the fine particles. Their average composition was 50 at% Ti , 28 at% Cr , 22 at% N . It is known that the lattice parameter of $(Ti,Cr)N$ decreases as Cr content increases. This appears to explain the lattice parameter value of fine particles which was located midway between TiN and CrN . Many reported relationships between the lattice parameter and Cr content of $(Ti,Cr)N$. Figure 6 summarizes the composition dependence of the lattice parameter. All data on Fig. 6 were taken from references.^{12,18,21,24,32)} The relationship between the lattice parameter and Cr content can be expressed as:

Fig. 2 (a) TEM micrograph and (b) diffractogram of a cubic- TiN nanoparticle produced by electrical explosion of Cr-coated Ti wire under 0.1013 MPa N_2 gas. The diffractogram was obtained by fast Fourier transformation.

Fig. 3 (a) TEM micrograph and (b) diffractogram of β -Cr₂N nanoparticle produced by electrical explosion of Cr-coated Ti wire under 0.1013 MPa N₂ gas. The diffractogram was obtained by fast Fourier transformation.

Fig. 4 (a) TEM micrograph, (b) high resolution image of fine nanoparticles produced by electrical explosion of Cr-coated Ti wire under 0.1013 MPa N₂ gas and a diffractogram of a dotted region, (inset). The diffractogram on the inset of Fig. 4(b) shows that the corresponding center region of the sample holds the cubic symmetry. (c) A pattern of rings obtained by fast Fourier transformation of the whole region in Fig. 4(b).

Fig. 5 (a) STEM image and (b) EDS spectrum of fine particles produced by electrical explosion of Cr-coated Ti wire under 0.1013 MPa N₂ gas. Cu peaks generated from the carbon-coated copper grid are not indicated.

$$a(\text{nm}) = 0.4234 - 0.000081 x \quad (1)$$

Here, x is the atomic percent of Cr (at% Cr).

If one puts the measured value of 0.4206 nm in this study in eq. (1), we get 34.5 at% Cr. It is slightly higher than that

we measured by EDS (28 at%). Nevertheless, this is an acceptable agreement considering the experimental uncertainties involved in this kind of experiment. In any case, it appears reasonable to assume that the fine particles are (Ti,Cr)N in view of EDS and lattice parameter value. To

Fig. 6 Variation of lattice parameter of (Ti,Cr)N with Cr content.^{12,18,21,24,32)}

conclude, TiN, Cr₂N, and (Ti,Cr)N phases were synthesized by the electrical wire explosion of Cr-coated Ti wires in N₂ gas.

Acknowledgement

This research was supported by the Basic Research Project of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Knowledge Economy of Korea.

REFERENCES

- 1) H. Kudo and O. Odawara: *J. Mater. Sci.* **24** (1989) 4030–4033.
- 2) M. Shibuya, J. F. Despress and O. Odawara: *J. Mater. Sci.* **33** (1998) 2573–2576.
- 3) R. M. Marin-Ayral, C. Pascal, F. Martinez and J. C. Tedenac: *J. Eur. Ceram. Soc.* **20** (2000) 2679–2684.
- 4) Z.-H. Chin and T.-P. Perng: *Appl. Phys. Lett.* **70** (1997) 2080–2382.
- 5) G. V. White, K. J. D. Mackenzie and J. H. Johnston: *J. Mater. Sci.* **27** (1992) 4287–4293.
- 6) G. W. Elger, D. E. Traut, G. J. Slavens and S. J. Gerdemann: *Metall. Trans. B* **20B** (1989) 493–497.
- 7) D. T. Castro and J. Y. Ying: *Nanostruct. Mater.* **9** (1997) 67–70.
- 8) J. L. H. Chau and C. C. Kao: *Mater. Lett.* **61** (2007) 1583–1587.
- 9) W. Kim, J.-S. Park, C. Y. Suh, S. W. Cho, S. Lee and I. J. Shon: *Mater. Trans.* **50** (2009) 2897–2899.
- 10) H. A. Jehn, F. Thiergarten, E. Ebersbach and D. Fabian: *Surf. Coat. Technol.* **50** (1991) 45–52.
- 11) Ch. Wirz, A. Blatter and R. Hauert: *Thin Solid Films* **214** (1992) 63–67.
- 12) Y. Massiani, P. Gravier, L. Fedrizzi and F. Marchetti: *Thin Solid Films* **261** (1995) 202–208.
- 13) Y. Otani and S. Hofmann: *Thin Solid Films* **287** (1996) 188–192.
- 14) J. J. Nainaparampil, J. S. Zabinski and A. Korenyi-Both: *Thin Solid Films* **333** (1998) 88–94.
- 15) H. Hasegawa, A. Kimura and T. Suzuki: *Surf. Coat. Technol.* **131** (2000) 76–79.
- 16) K. H. Lee, C. H. Park, Y. S. Yoon and J. J. Lee: *Thin Solid Films* **385** (2001) 167–173.
- 17) D. B. Lee, M. H. Kim, Y. C. Lee and S. C. Kwon: *Surf. Coat. Technol.* **141** (2001) 232–239.
- 18) K. H. Lee, S. J. Jung, J. J. Lee and C. Park: *J. Mater. Sci. Lett.* **21** (2002) 423–425.
- 19) D. J. Jung, J. S. Park, H. D. Na, J. W. Lim, J. J. Lee and J. H. Joo: *Surf. Coat. Technol.* **169–170** (2003) 424–427.
- 20) J. G. Han, H. S. Myung, H. M. Lee and L. R. Shaginyan: *Surf. Coat. Technol.* **174–175** (2003) 738–743.
- 21) S. M. Aouadi, K. C. Wong, K. A. R. Mitchell, F. Namavar, E. Tobin, D. M. Mihut and S. L. Rohde: *Appl. Surf. Sci.* **229** (2004) 387–394.
- 22) V. V. Uglov, V. M. Anishchik, S. V. Zlotski, G. Abadias and S. N. Dub: *Surf. Coat. Technol.* **200** (2005) 178–181.
- 23) V. M. Vishnyakov, V. I. Bachurin, K. F. Minnebaev, R. Valizadeh, D. G. Teer, J. S. Colligon, V. V. Vishnyakov and V. E. Yurasova: *Thin Solid Films* **497** (2006) 189–195.
- 24) X. Jin, L. Gao and J. Sun: *Acta Mater.* **54** (2006) 4035–4041.
- 25) W. Kim, J. S. Park, C. Y. Suh, J. C. Lee, J. Kim and Y. J. Oh: *Mater. Trans.* **48** (2007) 1973–1974.
- 26) W. Kim, J. S. Park, C. Y. Suh, H. Chang and J. C. Lee: *Mater. Lett.* **61** (2007) 4259–4261.
- 27) W. Kim, J. S. Park, C. Y. Suh, J. G. Ahn and J. C. Lee: *J. Alloy. Compd.* **465** (2008) L4–L6.
- 28) W. Kim, J. S. Park, C. Y. Suh, S. W. Cho and S. Lee: *Mater. Trans.* **50** (2009) 2344–2346.
- 29) W. Kim, J. S. Park, C. Y. Suh, S. W. Cho, S. Lee and I. J. Sohn: *Mater. Trans.* **50** (2009) 2897–2899.
- 30) M. D. Lyutaya and O. P. Kulik: *Powder Metall. Met.* **13** (1974) 792–794.
- 31) A. Matsunawa and S. Katayama: *Trans. JWRI* **19** (1990) 137–148.
- 32) P. Hones, R. Sanjines and F. Levy: *Thin Solid Films* **332** (1998) 240–246.