Microstructure of Ti-Cr Nanoparticles Prepared by Electrical Wire Explosion

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The reaction products of electrical wire explosion with 25 at% Cr-coated Ti wire were identified as β -TiCr₂, α -Ti, β (Ti,Cr) and α -TiCr₂ based on the selected area electron diffraction patterns. There was a bimodal size distribution where Ti-Cr particles were 40–50 nm in size, and fine particles less than 10 nm were determined to be pure Ti or Cr. The Ti-Cr nanoparticles are not only a mixture of Ti-Cr phases but they are also heterogeneous themselves at a single particle level, due to the non-equilibrium effects of the EWE process. The very rapid collision and subsequent coalescence of Ti and Cr atom clusters are believed to have contributed to the formation of chemically segregated particles.

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1. Introduction

The electrical wire explosion (EWE) has been widely used in the manufacture of fine pure metals or alloy nanoparticles, such as Al-Si, Cu-Zn, Ni-Ti and Cu-Ni.^{1–4)} In pure single crystal titanium, the α -Ti (HCP) is transformed to β -Ti (BCC) at 882°C. Chromium is a beta stabilizer that depresses the transformation temperature and exhibits low alpha phase solubility (Fig. 1).⁵⁾ The EWE method was applied to the Ti-Cr alloy with 25 at% Cr-coated Ti wire. The XRD results reveal that the explosion products are α -Ti, TiCr₂ and the meta-stable Ti-rich β -phase of 13 at% Cr composition estimated from its lattice parameter.⁶⁾ The EWE results in a sharp change of the physical state of metal as a result of intense energy liberation when high-density current pulses run through it.⁷⁾ The complex transition of the wire material from a condensed state to a conducting plasma load is not yet understood completely.⁸⁾ Significant variation in the composition distribution of atoms in the final products of inter-metallic compounds has been reported in previous studies.^{2–4)} However, there are few reports on the chemical composition and microstructures of single alloy particles. In this study, the explosion products of Ti-Cr nanoparticles were examined with a FE-TEM, since a thorough investigation using a TEM could provide the evidence needed to interpret the reaction mechanism of the explosion.

2. Experimental Procedure

Specific details regarding the experimental procedure for manufacturing the Ti-Cr nanoparticles by EWE are described in Ref. 6). Ultrasonically-dispersed powder specimens in ethanol were mounted on a Cu grid coated with ultrathin carbon film. The specimens were examined by FE-TEM (Field-Emission Transmission Electron Microscope, model JEM-2010F, JEOL Ltd., Japan) operating at 200 kV at Korea Basic Science Institute. Z-contrast dark-field STEM imaging that use the HAADF (High-Angle Annular Dark-Field)

Fig. 1 Ti-Cr equilibrium diagram (Murray, 1981). The starting mixture composition of a Cr-coated Ti wire in this study is marked with a dotted line.

detector was conducted in order to investigate the chemical composition of individual Ti-Cr alloy nanoparticles produced by EWE, as well as by the conventional TEM techniques, such as BF (Bright Field) imaging and SAED (Selected Area Electron Diffraction).

3. Results and Discussion

Most of the Ti-Cr particles produced by EWE were 40–50 nm in size and fine particles less than 10 nm were pure Ti or Cr as a bimodal size distribution (Figs. 2(a) and 3). SAED and NBD (Nanobeam Diffraction) patterns were obtained for many single particles, but could hardly be indexed as belonging to the β (Ti,Cr) phase, which was aimed by the starting stoichiometry in the Ti-Cr equilibrium phases, as shown in Fig. 1. While the resolvable spotty rings in the SAED pattern gained by using a large selected area aperture were indexed as β -TiCr₂, α -Ti, β (Ti,Cr) and α -TiCr₂ by matching the measured d-spacings to the references

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Fig. 2 (a) BF image and (b) electron diffraction pattern of Ti-Cr alloy synthesized by the electrical wire explosion, showing the shape and size distribution of nano powders. The Miller indices for planes are indexed in Table 1 for each ring or reflection spot of the pattern.

Fig. 3 STEM-HAADF images and EDS spectra of (a) Cr and (b) Ti particles. Finer particles in Fig. 2(a) are unreacted Cr or Ti.

(Table 1). It was found that the reference d-spacings of each phase did not provide a good match to the measured d-spacings of the single phases in the SAED or NBD patterns. On the other hand, the diffraction contrast of large particles was partly varied across one particle, which indicates that

these grains were not likely a chemically homogeneous single phase (Fig. 4(a)). A HAADF-STEM image of a Ti-Cr particle shows the contrast difference with different Cr content ranging from 5.91 to 65.03 in at% obtained by using the EDS point analysis (Fig. 4(a)).

Fig. 4 (a) BF and (b) STEM-HAADF images of off-stoichiometric Ti-Cr particle. (b) Numbers are the Cr content in at% obtained by using the EDS point analysis. Ti and Cr are not homogeneously mixed but chemically segregated.

Table 1 Interplanar spacing and Miller indices of the possible phases for each ring in Fig. 2(b).

Reflection or Ring	d-spacing (nm)	Phase (hkl)
1	0.384	β -TiCr ₂ (102)
2	0.288	β -TiCr ₂ (104)
3	0.254	α -Ti (100) or β -TiCr ₂ (105)
4	0.232	α -Ti (002) or β -TiCr ₂ (106) or β (Ti,Cr) (110)
5	0.215	β -TiCr ₂ (200)
6	0.192	β -TiCr ₂ (203)
7	0.176	α -Ti (102) or β -TiCr ₂ (205) or α -TiCr ₂ (400)
8	0.158	β -TiCr ₂ (207) or α -TiCr ₂ (331) or β (Ti,Cr) (200)

The enthalpy of the formation of most intermetallic phases is relatively low and the product is often multi-phase, containing significant amounts of phases not intended by the starting stoichiometry when the reaction is thermally activated.⁹ The explosion in this study produced multi-phase nanoparticles, and each grain seemed to be off-stoichiometric Ti-Cr particles reflecting the non-equilibrium effects of the EWE process. However, our X-ray diffraction data revealed that the major phases are β (Ti,Cr), α -Ti and TiCr₂.⁶ The phases are the constituents of the eutectoid reaction (β (Ti,Cr) = α -Ti + α -TiCr₂). Therefore, it is obvious that eutectoid reaction plays an important role as well. The important thing is that the particles are not only a simple mixture of the Ti-Cr phases, but also heterogeneous themselves at a single particle level as in Fig. 4. Therefore, it can be said that β -TiCr₂, α -Ti, β (Ti,Cr), and α -TiCr₂ exist within the volume of the specimen defined by a selected area aperture, just as XRD averages the entire population in the bulk. That is why the indexing of SAED or NBD patterns for one grain was done with little success.

The shape of particles in Figs. 2(a) and 4(a) is not spherical, but round in a partly-distorted manner. The zoning features are also observed in Fig. 4(a). During the EWE, the metal is expanded into a biphasic state, which is compressed to the liquid state, exploded near the critical point, and condensed to a plasma state.⁷ It has been reported that the collision and subsequent coalescence of primary particles play an important role in the formation of nanoparticles in the gas phase after nucleation.¹⁰ A molecular dynamics simulation study has shown that the coalescence of nanoparticles happens so rapidly and gives rise to a strain in atoms near the void.¹¹ Molecular dynamics simulation also shows that the initial lattice orientations between two particles result in large deformations in three dimensions and a different shape of the nanoparticles.^{10,12} The features observed in Fig. 4 probably indicate that small clusters of Ti and Cr atoms experienced a collision and subsequent coalescence, and grew to big particles during the EWE process. Since Cr was coated on a Ti wire in this study, Ti and Cr atoms might have had a lower chance to mix with each other than when the alloy wire was used as the starting material. Fine particles might have moved more rapidly with less opportunity to collide with other particles due to the small collision cross-section, and remained as pure Ti or Cr particles. According to the study of the coalescence behavior of unequal sized silicon nanoparticles by classical molecular dynamics simulations that used the Stillinger-Weber potential, diffusion processes dominate the coalescence processes of near solid-like particles and no internal convection occurs at impact.¹⁰ Thus, it is assumed that there was not enough time for Ti and Cr atoms to be blended to form an intermetallic compound by diffusion. As a result, intermetallic alloying was not completely achieved via EWE and Ti and Cr atoms were not homogeneously mixed but chemically segregated, as shown in Fig. 4(a).

In summary, the explosion products of EWE with 25 at% Cr-coated Ti wire are comprised of multi-phases and

identified as β -TiCr₂, α -Ti, β (Ti,Cr) and α -TiCr₂ particles based on the selected area electron diffraction patterns. Most of the Ti-Cr particles produced by EWE were 40–50 nm in size and fine particles were pure with less than 10 nm Ti or Cr as a bimodal size distribution. The collision and subsequent coalescence of Ti and Cr atom clusters are considered to have given rise to the formation of chemically segregated nanoparticles. Fine particles might have moved more rapidly with less opportunity to collide with other particles and remain as pure Ti or Cr particles.

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