

Preparation of TiC-Ni nanocomposite powder by a metallothermic chloride reduction

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TiC-Ni nanocomposite particles were directly prepared by a newly-developed metallothermic chloride reduction process. The procedures of the process were composed of the transfer of a $\text{TiCl}_4 + 1/2\text{C}_2\text{Cl}_4$ solution into a Mg-Ni molten alloy, the formation of titanium carbides by the reaction between Ti and C atoms released by the Mg-reduction of the chloride and the vacuum separation of the vaporized Mg and MgCl_2 , thereby forming TiC-Ni nanocomposite particles with a uniform structure, about 100 nm in size. The stoichiometry of the titanium carbide in produced composite was approximately $\text{TiC}_{0.9}$, which is suitable for use in the tool industry.

Key words: Nanocomposite, Metallothermic reduction, Titanium carbide, Nanoparticles, Cermet.

Introduction

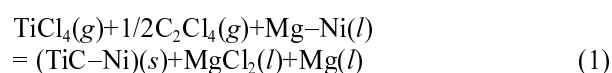
Composites of titanium carbide mixed with nickel have been widely used as cermet materials for production of various dies and tool parts [1-3]. To prepare such composite powders, an ordinary mixing of elemental micrometre-size particles has been usually employed in the tool industry. Since a higher mechanical strength of a part made with the composite powder can be easily achieved using elemental particles that are finer and more uniform, many studies on the production of high strength cermet materials have been focused on developing direct fabrication methods for a uniformly distributed fine composite powder. Among several methods, mechanical alloying has been a good route to produce such uniform composite powder although it has some drawbacks such as the contamination of the final product and the use of expensive high-purity raw powder materials [4, 5].

In this study, we attempted to fabricate nanostructured TiC-Ni composite powder by a new process utilizing magnesium thermal reduction [6]. In this process, gaseous metal chlorides (TiCl_4 and C_2Cl_4) reacted with a molten magnesium-nickel alloy and then the chlorides were reduced by the magnesium, forming stable MgCl_2 as a byproduct and releasing Ti and C atoms that subsequently formed TiC. The titanium carbides then reacted with Ni in the Ni-rich molten alloy, finally forming TiC-Ni composites. The residual liquid Mg and MgCl_2 were easily vaporized and fully removed during a vacuum separation. Characteristics of the synthesized TiC-Ni composite powder, such as phase uniformity, particle

size, composition of the TiC, and Ni content in the powder, were also investigated in this study.

Experimental

A solution of TiCl_4 (99.99 %) and C_2Cl_4 (99.96 %) was vertically fed to an insulated cylindrical mild-steel chamber (90 mm $\phi \times$ 180 mm L), in which a molten magnesium-nickel alloy was protected with Ar (1.1 atm). The reaction for the formation of a TiC-Ni composite can be generally expressed as follows:



In order to obtain one mole (60 g) of titanium carbide, the chloride solution was prepared by mixing 189.9 g of TiCl_4 and 41.5 g of C_2Cl_4 . The amount of magnesium needed for a full reduction of the chlorides was 97.2 g. However, an excess amount (250 g) of Mg-Ni alloy was prepared to prevent the formation of any intermediate phase such as TiCl_3 , TiCl_2 , or C_6Cl_6 . The nickel content in the alloys was 5, 12, and 18 wt %. The isolated chamber containing a Mg-Ni lump was heated to 473 K in vacuum. After filling with Ar (111.46 kPa), it was heated again to 1173 K to melt the lump. The chloride solution was then fed into the chamber at a feeding rate of 20 g/minute. After the reduction of the chlorides and the formation of TiC were completed, the residual Mg and MgCl_2 , which were easily vaporized, were fully removed by evacuating the chamber at 1.33 kPa for 3 hours at 1173 K so that the remaining Ni reacted with TiC to form TiC-Ni composites. The final product was a fragile sponge-shape bulk, which was easily pulverized to powder. The crushed powder was dissolved in an $\text{HF} + \text{HNO}_3$ solution and then free carbon in the powder was removed by filtering the solution. The carbon content in the powder was determined by subtracting

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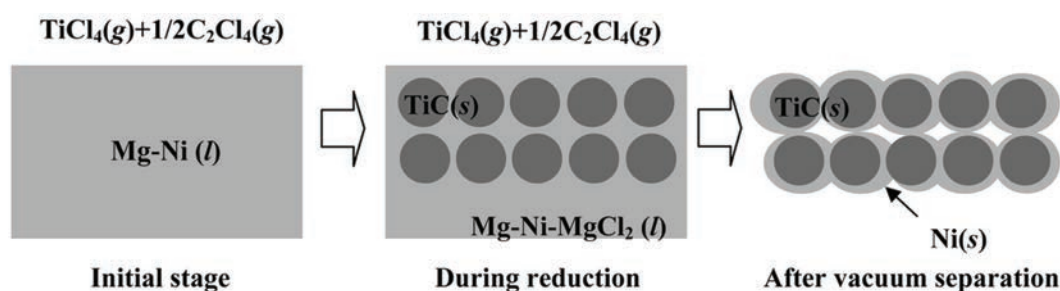


Fig. 1. Schematic illustration of the synthesis of TiC-Ni nanocomposite particles by metallothermal chloride reduction process.

Table 1. Equilibrium vapor pressures of the liquid phases remaining after the reduction step at 1173 K.

Phase	Mg(l)	MgCl ₂ (l)	Ni(l)
Vapor pressure (kPa)	1.87×10^3	9.41×10^2	6.67×10^{-7}

the amount of free carbon from the total amount of carbon. Impurities in the powder, such as Mg, Cl, Fe and O, were analyzed with a mass spectrometer (PQ2 Turbo ICP-MS) and a carbon-oxygen analyzer (LECO TC436). Phase analysis was performed by means of Cu $K\alpha$ X-ray diffraction (RIGAKU R2000) and a microstructural investigation was carried out with a SEM (HITACHI S4200) and a TEM (JEOL, JEM-2000EX).

Results and Discussion

A metallothermal chloride reduction process for the synthesis of TiC-Ni nanocomposite powder is schematically illustrated in Fig. 1. When the solution of $\text{TiCl}_4 + 1/2\text{C}_2\text{Cl}_4$ is transferred to the reaction chamber which contains a liquefied Mg-Ni alloy at 1173 K, it evaporates immediately to gaseous phases inside the chamber. The boiling points of TiCl_4 and C_2Cl_4 are 409 K and 396 K, respectively. These gases are then reduced by the magnesium in the Mg-Ni liquid, especially on the surface of the liquid, leading to the formation of MgCl_2 and subsequently releasing Ti and C atoms. The released Ti and C atoms are actively combined to form TiC particles and then the liquid MgCl_2 settles down to the bottom of the chamber due to the difference in density from that of the Mg-Ni liquid. The synthesized TiC particles are agglomerated to form a loose film on the surface of the Mg-Ni liquid. Also the film is kept wet by the Mg-Ni liquid due to the capillary effect, which makes a continuous reaction possible. Meanwhile, as the magnesium in the liquid Mg-Ni is continuously consumed to reduce the chlorides, Ni is highly concentrated in the liquid and encloses the TiC particles already formed. As the film becomes thicker and larger, it eventually settles down to the bottom of the chamber. The vapour pressures of the liquid Mg and the liquid MgCl_2 at 1173 K are very high, i.e., 1.87×10^3 kPa and 9.41×10^2 kPa, respectively, whereas that of the liquid Ni is only 6.67×10^{-7} kPa as shown in Table 1. Therefore, the residual Mg and MgCl_2 liquids can be fully removed

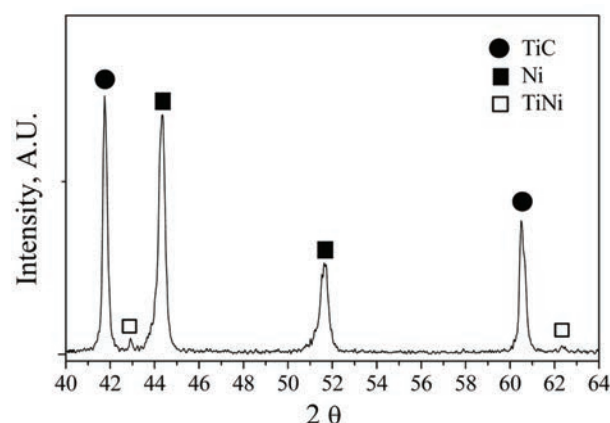


Fig. 2. X-ray diffraction pattern of TiC-Ni nanocomposite particles prepared by metallothermal chloride reduction process.

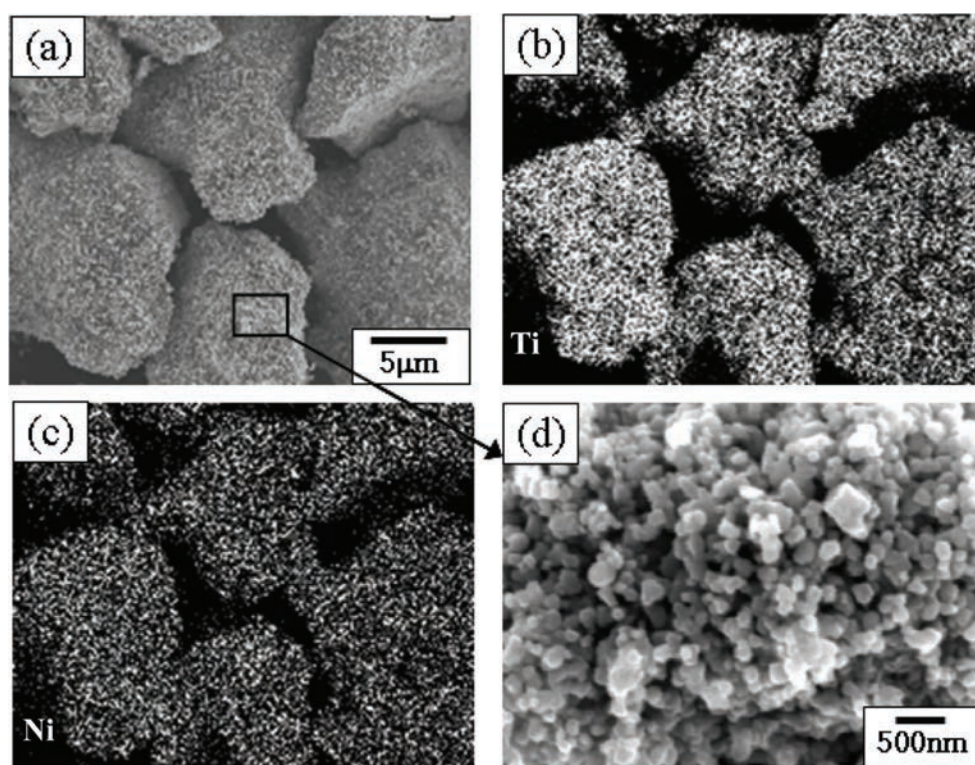
during vacuum separation at 1173 K, eventually leaving a fragile sponge-shape TiC-Ni composite that is easily pulverized to powder.

As shown in Fig. 2, the powder produced was crystalline and consisted of TiC, Ni, and small amount of TiNi. By chemical analyses, it was found that the composition of TiC in the TiC-Ni composites was approximately $\text{TiC}_{0.9}$. In general, the lattice parameter of titanium carbide is proportional to the carbon content in the carbide [7]. The lattice parameter of the TiC in the TiC-Ni composite powder, measured by an extrapolation technique, was 0.4327 nm, which is almost identical to the standard value of a stoichiometric TiC (JCPDS # 32-1383). Because the hardness of a sintered body is closely related to the carbon content in the TiC powder [8], it is important to maintain the composition of the TiC as near stoichiometric as possible. In fact, the composition of TiC in the composite powder synthesized in this study would satisfy the requirement ($\text{TiC}_{0.9\uparrow}$) of tool industry.

Results of the chemical analysis on the crushed TiC-Ni composite powder are summarized in Table 2. The amount of Ni in the initial Mg-Ni alloys (250 g each), calculated from the composition of the alloys, was 12.5, 30.0, and 45.0 g, respectively. Assuming that all the Ni in the Mg-Ni alloy reacts with one mole (60 g) of TiC to form a TiC-Ni nanocomposite powder, the nickel content in the powder should be 17.2, 33.3 and 42.9 wt%, respectively. As revealed in Table 2, the nickel contents in the powder synthesized were all similar to these values.

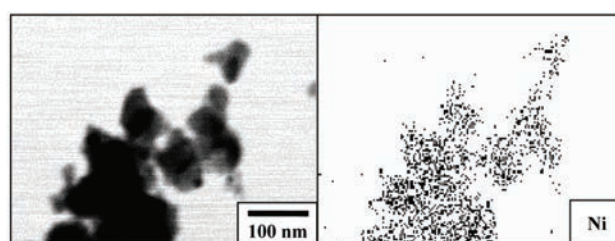
Table 2. Chemical compositions and carbon contents in TiC-Ni nanocomposite powder produced with various Mg-Ni reducers. (wt%)

	Reducer	Fe	Mg	Cl	O	Ni	Ti (Bal.)	C			X in TiC _x
								Total	Free	In TiC	
1	Mg-Ni 5%	2.73	0.25	0.32	0.8	19.8	62.3	13.8	0.3	13.5	0.89
2	Mg-Ni 12%	2.20	0.18	0.32	0.9	31.5	52.9	12.0	0.2	11.8	0.91
3	Mg-Ni 18%	3.10	0.22	0.28	0.9	40.2	45.1	10.2	0.2	10.0	0.91

**Fig. 3.** (a) SEM micrograph of a crushed TiC-Ni powder. (b) and (c) Element mapping of Ti and Ni in the powder shown in (a). (d) Closer look at the coarse particle in (a).

This indicates that the Ni content in the final product can be controlled by adjusting the composition of the initial Mg-Ni alloy. As listed in Table 2, impurities in the synthesized TiC-Ni composite powder were Fe 2.20-3.10 wt%, Mg 0.18-0.25 wt%, Cl 0.28-0.32 wt%, and oxygen 0.80-0.90 wt%, respectively. While Mg and Cl obviously originated from insufficient vacuum separation, Fe was diffused out from the mild-steel chamber. It is thought that Mg and Fe exist as stable oxides such as MgO and Fe_xO_y rather than as pure metals. Such impurities may be minimized by using a chemically more stable chamber, e.g., a Ti chamber and tight control of the vacuum separation process.

As shown in Fig. 3, Ti and Ni were uniformly distributed throughout the coarse particles of the TiC-Ni powder, indicating that TiC and Ni are mixed homogeneously in the powder (Fig. 3(b) and (c)). The coarse particle itself had a loose agglomerated structure with extremely fine TiC-Ni particles about 100 nm in size as shown in Fig. 3(d). In fact, as revealed in Fig. 4, TEM investigation of the microstructure revealed that each particle in Fig. 3(d)

**Fig. 4.** TEM micrograph of TiC-Ni composite particles and the distribution of Ni in the particles.

consisted of one or more subparticles that had a core/shell type structure in which the TiC core was enclosed with a Ni layer. This indicates that the powder synthesized is not a simple mixture of individual TiC and Ni nanoparticles, but is truly composed of TiC-Ni nanocomposite particles. Mechanical properties of the TiC-Ni nanocomposite powder are being studied.

It should be noted that the process introduced in this study can be applied to fabricate more complicated nanostructured carbides and composites. For example, composites of

Ta/Nb/V/W-C/N + Ni/Co/Al can be directly fabricated at temperatures lower than 1273 K by choosing the appropriate metal chlorides such as TaCl_5 , NbCl_5 , VCl_4 , and WCl_5 and the binary alloys such as Mg-Ni, Mg-Co and Mg-Al alloys as reducers. Fabrication of WC-Co nanocomposite powder, based on the reaction $\text{WCl}_5(g) + \text{C}_2\text{Cl}_4(g) + \text{Mg-Co}(l) = (\text{WC} + \text{Co})(s) + (\text{Mg} + \text{MgCl}_2)(l)$, is being carried out.

Conclusions

Titanium carbide-nickel nanocomposite powders were successfully prepared by a metallothermic chloride reduction process. The procedures of the process were composed of the transfer of a $\text{TiCl}_4 + \text{C}_2\text{Cl}_4$ solution into a Mg-Ni molten alloy, the magnesium reduction of the chlorides, the formation of titanium carbide by the reaction between Ti and C atoms released by the reduction, and the vacuum separation of the residual Mg and MgCl_2 , thereby forming TiC-Ni nanocomposites by enclosing TiC with the remaining Ni. The powder produced had a loose agglomerated structure with extremely fine TiC-Ni particles about 100 nm in size. Each particle had a core/shell type structure such that the TiC core was enclosed with a Ni layer. The composition of TiC in the powder was approximately $\text{TiC}_{0.9}$, which is suitable for use in the tool industry.

Acknowledgements

This research was supported by a grant from the "Korea Energy Management Corporation (KEMCO)" in Korea.

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