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EXTRACTION FACTOR OF TUNGSTEN SOURCES FROM TUNGSTEN SCRAPS BY ZINC DECOMPOSITION PROCESS

WSPÓŁCZYNNIK EKSTRAKCJI ZWIĄZKÓW WOLFRAMU Z ODPADÓW WOLFRAMOWYCH W PROCESIE ROZKŁADU CYNKU

Decomposition promoting factors and extraction process of tungsten carbide and tungstic acid powders in the zinc decomposition process of tungsten scraps which are composed mostly of tungsten carbide and cobalt were evaluated. Zinc volatility was suppressed by the enclosed graphite crucible and zinc volatilization pressure was produced in the reaction graphite crucible inside an electric furnace for ZDP (Zinc Decomposition Process). Decomposition reaction was done for 2hours at 650°, which 100% decomposed the tungsten scraps that were over 30 mm thick. Decomposed scraps were pulverized under 75μm and were composed of tungsten carbide and cobalt identified by the XRD (X-ray Diffraction). To produce the WC(Tungsten Carbide) powder directly from decomposed scraps, pulverized powders were reacted with hydrochloric acid to remove the cobalt binder. Also to produce the tungstic acid, pulverized powders were reacted with aqua regia to remove the cobalt binder and oxidize the tungsten carbide. Tungsten carbide and tungstic acid powders were identified by XRD and chemical composition analysis.

Keywords: Raw material, Recycling, Zinc decomposition process, Tungsten carbide, Tungstic acid

1. Introduction

The recycling of tungsten scraps has been considered primarily based on hydrometallurgy or hydrothermal treatment methods [1]. Venkateswaran et al. introduced a melt bath technique to convert tungsten scraps to tungsten carbide powder [2]. Selective removal of cobalt binder from tungsten scraps for recycling has been attempted using an acid solution with additives, acetic acid leaching, and a hydrothermal extraction process [3-5]. These physical and chemical methods are used to recover tungsten sources, with or without the removal of the cobalt binder.

In tungsten scraps, cobalt which acts as a binder is decomposed-separated from tungsten scraps in a high temperature zinc melting alloy to directly obtain tungsten carbide-cobalt powder. This is called as the zinc decomposition process (hereinafter ZDP) [6-9]. The technology of the zinc method of processing tungsten scraps developed by the Mining Bureau of the United States in the early 1970s still finds wide application for regeneration of the wastes of solid alloys of the VK type consisting of tungsten carbide and cobalt [10]. In the zinc process, molten zinc is initially alloyed with the cobalt phase of the tungsten scraps. Upon subsequent removal and recovery of the zinc by distillation, a porous tungsten carbide-cabalt lump remains [11]. The lump was pulverized and reground, and blended for pressing and sin-

tering into new products. Studies on tungsten scrap recycling of ZDP mentioned the basic decomposition reaction, but they lack discussions on the decomposition promoting factors and decomposition mechanism of tungsten scraps. Many studies focused on the leaching of cobalt and formation of tungstic acid simultaneously during the aqua regia (hydrochloric acid and nitric acid) treatment of the tungsten scraps [12-13]. Also they could not produce the tungsten carbide powders without cobalt directly from tungsten scraps through ZDP.

In this study, decomposition promoting conditions and mechanism of tungsten scraps only composed of WC-Co was evaluated through ZDP. Also, the high-purification process through chemical treatment of recycled powders from ZDP was assessed to produce tungsten carbide and tungstic acid powders from zinc reacted powders composed of tungsten carbide and cobalt.

2. Experimental

Tungsten scraps used in this experiment were cylindrical type with a diameter of 40 mm and height of 20 mm as seen in Fig. 1(a). The composition rate of tungsten carbide is 92.76% and 7.24% was cobalt. The tungsten carbide particle size was about 0.8~1.5 μm as in Fig. 1(b). Main crystal phase was analyzed as tungsten carbide (Fig. 1(c)).

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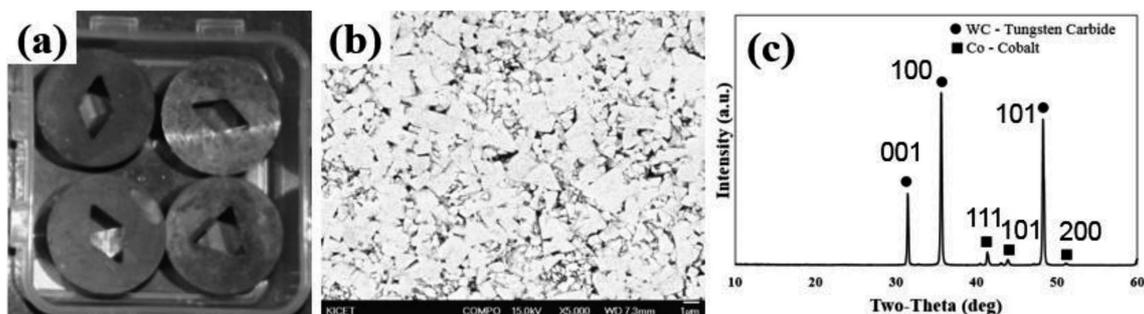♯   Corresponding author: pee@kicet.re.kr

Fig. 1. External appearance of tungsten scraps (a), microstructure (b) and crystal phase analysis (c)
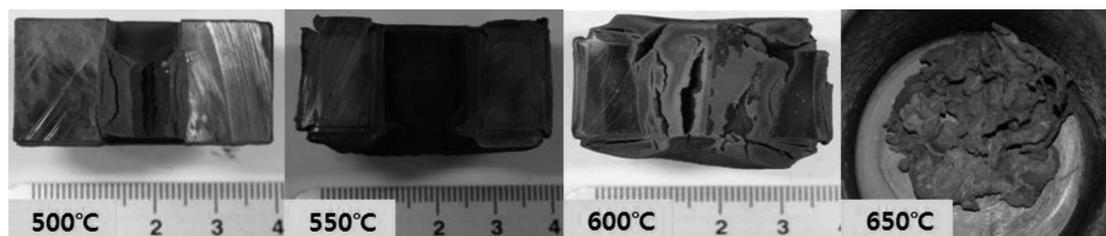

Fig. 2. Decomposition state of tungsten scraps depending on ZDP reaction temperature for 2 hours

The amount of zinc input for ZDP reaction was set at a ratio of 1:3 and 1:4 compared to the scrap weight. The reaction temperature in the experiment was set at a range of 500~650° which is higher than the melting point of zinc. The atmosphere of the electric furnace for ZDP was controlled with argon gas. Pressure within the electric furnace was made into a vacuum state with a vacuum pump, or argon gas was injected at 5 l/min to maintain near air pressure. Also, the reaction graphite crucible was manufactured into a sealed structure so that zinc steam pressure was generated inside the crucible. With the decantation process, zinc melted alloy with some cobalt melted was separated from the crucible where ZDP reaction was completed. The sealed cover was designed so that it could be automatically separated during the decantation process. In order to remove zinc remaining in the completely decomposed tungsten carbide-cobalt mass (aggregation), it was reheated up to 1000°, maintained for 1 hour and the remaining zinc was almost completely volatilized. In order to evaluate the reaction state of each condition in ZDP, the products were cut into half with a diamond cutter. The reacted layer thickness was measured and the decomposition rate was calculated. The decomposed lumps of scraps were crushed with a mortar to obtain tungsten carbide-cobalt powder. XRD (X-ray diffraction, Right D/max 2500v/pc, Rigaku, Japan) was used for crystal phase analysis of the powder, and SEM (JSM-6390, JEOL, Japan) was used to observe microstructures. Composition analysis was done with EDS (7421 Resol at 5.9 KeV, Oxford instruments, England) and XRF (ZSX Primus, Rigaku, Japan) and ICP-OES (PerkinElmer 5300 DV).

100g of recycled tungsten carbide-cobalt powder through ZDP was eluted for 12 hours at 60° in 500 ml of hydrochloric acid and aqua regia in order to completely remove cobalt and zinc remaining in the recycled powder. A reflux condenser was attached to prevent the evaporation of the solution. At first, 500 ml hydrochloric acid and aqua regia solutions of pre-determined concentration was poured into the flask. Then, 100 g of recycled tungsten carbide and cobalt powders which was pulverized under 75 μm were charged in the vessels and heated rapidly at 60°. The reaction vessels were agitated until the end of the experiment. After completing the reaction, the solution and residue were separated using a centrifuge and washed several times. The residue was dried and characterized by XRD and SEM.

3. Results and discussion

Fig. 2 shows cross sections of reactants obtained from ZDP. In the ZDP, zinc and tungsten scraps at an input ratio of 1:4 inside a sealed graphite crucible in which zinc steam pressure was generated were put. Reaction was progressed for 2 hours by ZDP temperature. Fig. 2 shows that the thickness of the decomposition layer thickens as reaction temperature rises. Specimen that reacted for 2 hours at 650° appeared to be collapsed instead of being cylindrical type since the tungsten scrap structure was completely destroyed.

The zinc input ratio was set as 1:3, 1:4 in which the tungsten scraps completely sink inside melted zinc. The eutectic reaction of cobalt and zinc became active as the reaction temperature increased. The liquid forming velocity of solid phase cobalt increased, promoting decomposition of tungsten scraps. Also, the high decomposition rate when zinc input amount was 1:4 could be caused from rapid diffusion melting of tungsten scrap cobalt to melted zinc. The graphite crucible inside the electric furnace was a sealed structure, so that the zinc volatilization could not escape outside the reaction crucible. This zinc volatilization pressure increases inside the reaction crucible as reaction temperature increases [14]. The high zinc volatilization pressure is thought as zinc melting alloy promoting penetration into the tungsten scraps. As a result, the decomposition rate of tungsten scraps increased as seen in Fig. 3. From this, the decomposition of tungsten scraps was promoted and we realized that 100% decomposition could be enabled from 2 hours of reaction at 650°.

In the crystal phase analysis result on powder made from a lump obtained after ZDP reaction, most were tungsten carbide peaks and some cobalt peaks existed near 42 degrees. Zinc used in ZDP did not appear in the crystal phase analysis. Although the tungsten scrap structure collapsed in ZDP, tungsten carbide powder aggregations of $1 \sim 40 \ \mu$m were observed. Magnified observations showed that cobalt which acts as a binder of waste hard metals still existed inside. The particle size of tungsten carbide was seen to maintain its initial state of about $0.8 \sim 1.5 \ \mu$m. In XRF analysis results of these powders, tungsten carbide was measured as 91.32% and cobalt as 6.89%. Although zinc was volatized at 1000° for 1hour, XRF analysis results showed that 1.79% of zinc still remained.
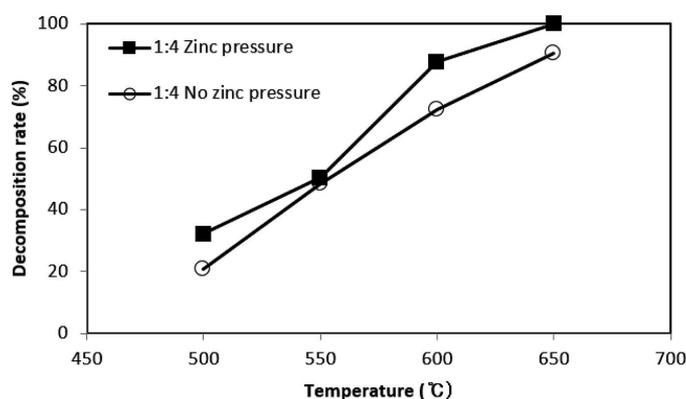

Fig. 3. Decomposition rate of tungsten scraps depending on zinc volatilization pressure

Liquid zinc meets cobalt which is a binder of tungsten carbide, and forms a cobalt-zinc melted alloy first through the eutectic reaction. This melted alloy expanded the volume, and was considered to promote continuous penetration of liquid zinc along the cobalt layer. That is, a cobalt-zinc melted alloy was formed in the cobalt layer which existed between tungsten carbides. Tungsten scraps were separated in a layered form from the basic material [11]. Due to this melted alloy, the solid cobalt layer transform into liquid so that their volume was expanded and the gap between tungsten carbide particles widened, enabling zinc to penetrate. Tungsten carbide formed layers and was separated from the hard metal basic material [11].

Zinc has to be removed since it interferes with recycled tungsten carbide and cobalt powders during sintering process. Also to produce pure tungsten carbide powder or tungstic acid from recycled powder through ZDP, chemical treatment is need. Zinc and cobalt removal was done with hydrochloric acid solution. Lumps obtained from ZDP were crushed into powders (under $75 \ \mu$m). Then powders were eluted in hydrochloric acid solution at 60° for 2 hours in order to remove the zinc and cobalt remaining in the powders. After washing process, the composition of residual tungsten carbide powder obtained after acid processing was analyzed with XRF. Zinc was <0.01% and cobalt was <0.01%. Fig. 4 (a) shows the crystal phase analysis of powder obtained from hydrochloric acid extraction process. Tungsten carbide peaks mostly appeared. It was confirmed that tungsten carbide was not oxidized even during hydrochloric acid extraction processing. Fig. 4(b) is microstructure of powders after hydrochloric acid extraction processing. Tungsten carbide particles are aggregated to about

$1 \sim 6 \ \mu$m. Some tungsten carbide particles are separated from each other as their binder cobalt melted away due to the hydrochloric acid extraction process.

The leaching of tungsten carbide and formation of tungstic acid simultaneously during the aqua regia (three parts hydrochloric acid and one part nitric acid) extraction process of the recycled tungsten carbide powder can be broadly expressed as follows [13]:

$$HNO_3 + 3HCl = NOCl + 2H_2O + Cl_2 \qquad (1)$$

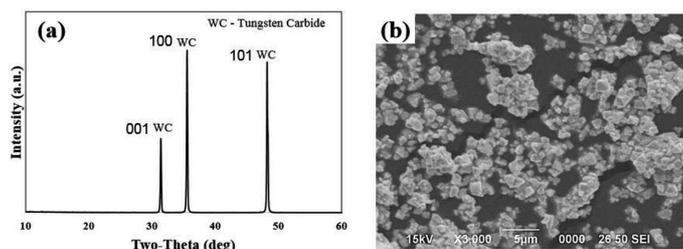$$WC + 5HNO_3 + 5HCl = H_2WO_4 + CO_2 + 5NOCl + 4H_2O \quad (2)$$

Fig. 4. XRD pattern (a) and microstructure (b) of powder obtained from hydrochloric acid extraction process

To produce a pure tungstic acid powder from recycled pure tungsten carbide powder, recycled tungsten carbide powder was eluted by aqua regia solution. Fig. 5(a) shows the XRD pattern of powder obtained from aqua regia extraction process. Tungstic acid peaks mostly appeared. It was confirmed that tungsten carbide was fully oxidized during aqua regia extraction process. Fig 5(b) is microstructure of powders after aqua regia extraction processing. Tungstic acid particles are aggregated to about $5 \sim 80 \ \mu$m. In the results of chemical analysis of tungstic acid powder obtained from aqua regia extraction process, the major metal impurities in tungstic acid are silicone (210 ppm), Ta (110 ppm), Nb (203 ppm) and the purity of tungstic acid is found to be 99.94%.
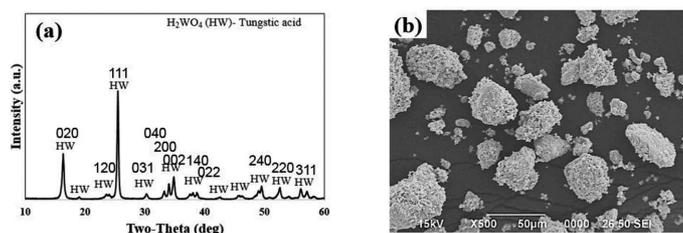

Fig. 5. XRD pattern (a) and microstructure (b) of powder obtained from aqua regia extraction process

4. Conclusions

Decomposition promoting factors and extraction process of tungsten carbide and tungstic acid powders in the zinc decomposition process of tungsten scraps which are composed mostly of tungsten carbide and cobalt were evaluated. Zinc volatility was suppressed by the enclosed graphite crucible and zinc volatilization pressure was produced in the reaction graphite crucible inside an electric furnace for ZDP. Decomposition reaction was done for 2hours at 650°, which 100% decomposed the tungsten scraps that were over 30 mm thick.

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Decomposed scraps were pulverized under 75 μm and were composed of tungsten carbide and cobalt identified by the XRD. To produce the tungsten carbide powder directly from decomposed scraps, pulverized powders were eluted by hydrochloric acid process to remove the cobalt binder and zinc. Also to produce the tungstic acid, pulverized powders were reacted with aqua regia to remove the cobalt binder and oxidized. Tungsten carbide and tungstic acid powders were identified by XRD and chemical composition analysis.

Acknowledgements

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