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CHULWOONG HAN*, HYUNWOONG NA**, HANSHIN CHOI*, YONGHWAN KIM*,♯

HIGH PURITY TUNGSTEN SPHERICAL PARTICLE PREPARATION FROM WC-Co SPENT HARD SCRAP

WYTWARZANIE WYSOKIEJ CZYSTOŚCI SFERYCZNYCH CZĄSTEK WOLFRAMU Z TWARDEGO ZŁOMU WC-Co

Tungsten carbide-cobalt hard metal scrap was recycled to obtain high purity spherical tungsten powder by a combined hydrometallurgy and physical metallurgy pathway. Selective leaching of tungsten element from hard metal scrap occurs at solid / liquid interface and therefore enlargement of effective surface area is advantageous. Linear oxidation behavior of Tungsten carbide-cobalt and the oxidized scrap is friable to be pulverized by milling process. In this regard, isothermally oxidized Tungsten carbide-cobalt hard metal scrap was mechanically broken into particles and then tungsten trioxide particle was recovered by hydrometallurgical method. Recovered tungsten trioxide was reduced to tungsten particle in a hydrogen environment. After that, tungsten particle was melted and solidified to make a spherical one by RF (Ratio Frequency) thermal plasma process. Well spherical tungsten micro-particle was successfully obtained from spent scrap. In addition to the morphological change, thermal plasma process showed an advantage for the purification of feedstock particle.

Keywords: WC-Co, spent hard scrap, hydrometallurgy, RF thermal plasma

1. Introduction

Tungsten element belongs to rare metals as natural resources are rare and mal-distributed in the world. Moreover, world production is highly centered to a few countries [1]. In order to secure tungsten supply in industries, secondary resources such as scraps and end-of-life products should substitute primary resources. Therefore, it has been challenging to proliferate reuse and recycling technology of scraps with higher material efficiency as well as energy efficiency. A significant amount of tungsten has been consumed to make hard metal tools in tungsten mass flow [2]. Besides, high purity tungsten over 99.99% is used for interconnection. In most cases, recycling of hard metal scraps follows a close loop circulation where scraps from hard metals are recycled to tungsten carbide for hard metals [1]. In order to improve stability of tungsten recycling industries, recycling pathways need to be further diversified. In this context, a combined recycling pathway for spent hard metal tool is designed and the feasibility of the process was evaluated in this study. The suggested process is composed of hydrometallurgy and physical metallurgy. Tungsten trioxide (WO_3) was hydro-metallurgically recovered from WC-Co hard scrap by chemical reactions. After that, spherical tungsten micro-particle was obtained by physical reactions including reduction and subsequent thermal plasma spheroidization of WO_3 in order to obtain high purity tungsten powder.

2. Experimental procedure

Fig. 1. shows the process flow of the combined recycling from spent hard metal scrap to tungsten micro-particle. A straight type WC-12 wt.% Co hard scrap was isothermally oxidized at 800° for 10 hours and the fully oxidized scrap was mechanically broken into particles by hammer milling and jet milling. Tungsten was selectively dissolved from oxide mixture by sodium hydroxide with mechanical stirring. Co-containing solid was removed by filtering and then $CaWO_4$ was precipitated by adding calcium chloride. $CaWO_4$ was dissolved in hydrochloric acid and tungstic acid was obtained. Dehydrated WO_3 was reduced by hydrogen in a reducing furnace at C for hours. Tungsten particle was spheroidized by RF thermal plasma process as following the experimental condition of Table 1. Materials in the process were characterized in view of morphology, chemical composition, and phase composition. In the case of the chemical composition, glow discharge-mass spectroscopy (GD-MS) was conducted.

* INCHEON REGIONAL DIVISION (KOREA INSTITUTE OF INDUSTRIAL TECHNOLOGY, INCHEON, KOREA)
** DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING, YONSEI UNIVERSITY, SEOUL, KOREA
♯ Corresponding author: yhkim@kitech.re.kr

TABLE 1

Process parameters of RF thermal plasma spheroidization

Feedstock		Plasma power	Plasma gas					
Weight fraction WO_3	Feed-rate		Pressure	Central gas	Carrier gas	Sheath gas	Sheath gas	Quench gas
100g	5 g·min^{-1}	28 kW	14.7 psia	Ar 15slpm	Ar 5slpm	Ar 60slpm	H_2 10slpm	N_2 100slpm

3. Results and Discussion

Oxide powder was obtained by isothermal oxidation and subsequent milling process of WC-Co hard metal scrap and the characteristic features are shown in Fig. 1. A typical microstructure where tungsten carbide particles are embedded in metallic cobalt binder phase is observed in the as-received hard metal scrap as shown in Fig. 2 (a). Dense WC and Co phase mixture is transformed to porous WO_3 and $CoWO_4$ phase mixture by isothermal oxidation process owing to high Pilling-Bedworth ratio of components [3] and CO_2 gas formation [4]. When it comes to the isothermal oxidation kinetics, WC-Co showed a linear oxidation behavior and the kinetic parameter is increased with isothermal oxidation temperature increasing. Meanwhile, it is known that sublimation of tungsten oxide becomes substantial and it results in the mass loss of tungsten during oxidation [5]. Isothermal oxidation is advantageous for particle comminution. Particle size affects the kinetics of subsequent chemical reaction because effective surface area of chemical reaction is enlarged by the particle size reduction. Mean particle size of pulverized oxide scrap was um and cross-sectional morphology of the oxide scrap powder is shown in Fig. 2 (d). Describe the milled particle Jet milled WO3-CoWO4 particles was immersed in sodium hydroxide solvent at 90 ° where WO_4^{2-} ion is stable. The digestion reaction is simply described as following equations.

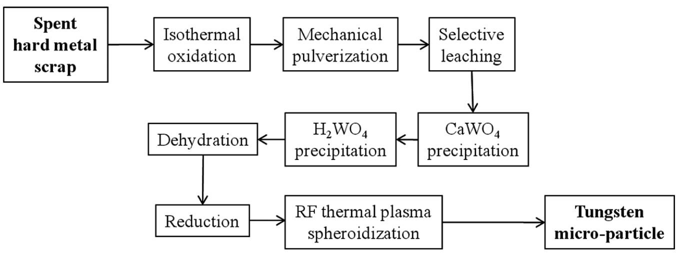
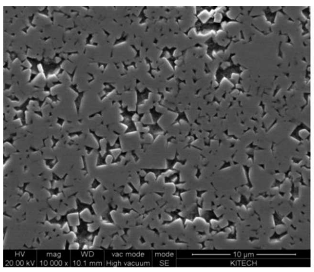
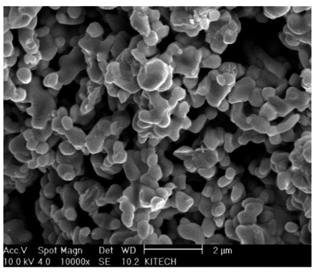


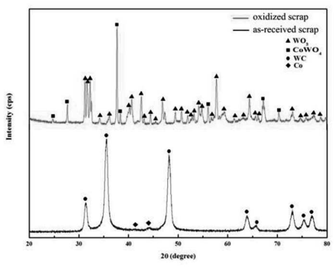
Fig. 1. Process flow of the combined recycling process



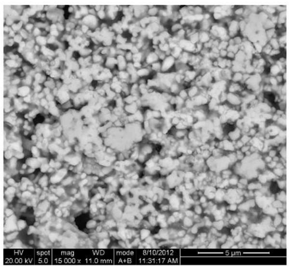
(a) Microstructure of as-received scrap



(b) Microstructure of oxidized scrap



(c) X-ray diffraction patterns



(d) Mechanically pulverized oxide scrap

Fig. 2. Characteristic features of as-received scrap, oxidized scrap, and pulverized oxide scrap

$$WO_3 + 2NaOH \rightarrow H_2O + Na_2WO_4 \quad (1)$$

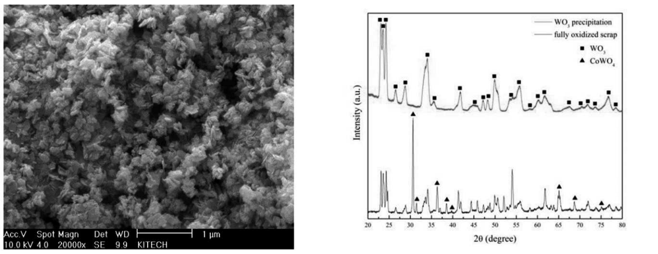
$$CoWO_4 + 2NaOH \rightarrow Co(OH)_2 \downarrow +2Na_2WO_4(2) \quad (2)$$

Sediment containing cobalt, cobalt hydroxide ($Co(OH)_2$), can be removed by vacuum filtering. $CaCl_2$ is added to sodium tungstate (Na_2WO_4) solution in order to precipitate calcium tungstate ($CaWO_4$) as shown in Eq. (3) after adjusting pH to be 10. Filtered $CaWO_4$ is re-dissolved by HCl at 50°C with stirring and accordingly tungstic acid (H_2WO_4) precipitates in strong acid solution by ion exchange Eq. (4). Washing and filtering step was repeated for 3 times using de-ionized water. Morphological change and phase composition change at each stage can be seen in Fig. 3.

$$Na_2WO_4 + CaCl_2 \rightarrow CaWO_4 \downarrow +2NaOH \quad (3)$$

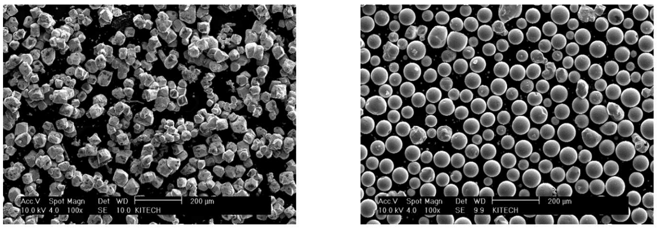
$$CaWO_4 + 2HCl \rightarrow CaCl_2 + H_2WO_4 \downarrow \quad (4)$$

In order to investigate reduction behavior of tungsten trioxide, thermo-gravimetric analysis was conducted with Ar and H_2 gas mixture flowing. Hydro-metallurgically prepared tungsten trioxide particle was reduced in a reducing environment and resulting tungsten particle morphology can be seen in Fig. 4(a). Aggregated particle with bulky primary particles is a typical morphology of tungsten from solid state reduction of tungsten oxide [6]. Mean particle size of reduced tungsten was um. The reduced tungsten particle was fed into thermal plasma. Particles individually react with thermal plasma during flight. Particles are heated and melt in the heating stage owing to high energy density of thermal plasma. Molten droplet solidifies to spherical form in order to reduce surface energy during cooling stage. Spherical tungsten particles are obtained in accordance with the melting and solidification pathway [7]. Reduced tungsten has a stable α-W phase while spheroidized tungsten consists of α-W phase and β-W phase. Meta-stable β-W phase results from the condensed nano-particles which covers the surface of spherical micro-particle [8].

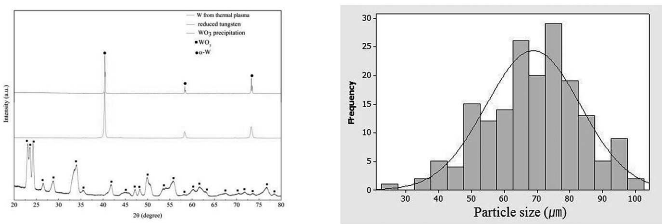


(a) WO_3 powder from hydrometallurgy (b) Phase evolution during WO_3 preparation

Fig. 3. Evolution of microstructure and phase composition of hydro-metallurgically recovered WO3 powder



(a) Reduced tungsten particle (b) Thermal plasma spheroidized W particle



(c) Phase composition (d) Size distribution

Fig. 4. Morphology of reduced tungsten particle and RF thermal plasma spheroidized one

TABLE 2

Chemical composition of hydro-metallurgically recovered WO_3 particle and thermal plasma spheroidized tungsten particle

Powder / Element	Impurity (ppm)							W
	Na	Al	Si	Ca	Fe	Co	Mo	
Reduced tungsten	360	130	1.000	1.000	34	18	3.2	Matrix
Spherical tungsten	1.4	3.2	4.3	6.7	1.5	2.1	3.4	matrix

* Reduced tungsten refers to the tungsten which was obtained from the reduction of tungsten oxide while spherical tungsten refers to the spheroidized tungsten by RF thermal plasma

In addition to morphological change, purification of feedstock is another advantage of thermal plasma spheroidization process. Glow discharge-mass spectroscopy was conducted for both tungsten particle after solid state reduction of recovered WO_3 and the other tungsten particle after RF thermal plasma spheroidization. Chemical composition change between reduced tungsten particle and spheroidized one is compared in Table 2. In the RF thermal plasma process, impurities having boiling temperature lower than in-flight particle temperature are removed from molten tungsten droplet by vaporization [9]. Indeed, the concentration of low boiling point elements in the spheroidized tungsten is markedly reduced when it is compared to that of reduced tungsten. Meanwhile, limitation in removing Mo, a refractory metal impurity, is observed. Through the results, it can be confirmed that spheroidization as well as purification is achieved by thermal plasma treatment.

4. Conclusion

A combined recycling pathway from WC-Co spent hard scrap to high purity spherical tungsten powder was designed and the process feasibility was evaluated in this study. Fully oxidized scrap is so friable to be easily broken into fine particle by mechanical pulverization process. Tungsten oxide particle was obtained from oxidized scrap through the hydrometallurgical process following selective leaching by NaOH, $CaWO_4$ precipitation with $CaCl_2$, and H_2WO_4 precipitation by HCl. Tungsten oxide particle was reduced to aggregated tungsten particle by solid-state reduction. Finally, spherical and high purity tungsten micro-particle was successfully obtained by RF thermal plasma process. In conclusion, the suggested combined recycling process showed a high feasibility for recycling spent WC-Co hard metal scraps.

Acknowledgements

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