ARCHIVES OF METALLURGY AND MATERIALS
Volume 60 2015 Issue 2
DOI: 10.1515/amm-2015-0141

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EXTRACTION FACTOR OF PURE AMMONIUM PARATUNGSTATE FROM TUNGSTEN SCRAPS

WSPÓŁCZYNNIK EKSTRAKCJI CZYSTEGO PARAWOLFRAMIANU AMONU Z ODPADÓW WOLFRAMOWYCH

Typical oxidation process of tungsten scraps was modified by the rotary kiln with oxygen burner to increase the oxidation rate of tungsten scraps. Also to accelerate the solubility of solid oxidized products, the hydrothermal reflux method was adapted. By heating tungsten scraps in rotary kiln with oxygen burner at around 900° for 2hrs, the scraps was oxidized completely. Then oxidized products (WO_3 and $CoWO_4$) was fully dissolved in the solution of NaOH by hydrothermal reflux method at 150° for 2hrs. The dissolution rate of oxidized products was increased with increasing the reaction temperature and concentration of NaOH. And then $CaWO_4$ and H_2WO_4 could be generated from the aqueous sodium tungstate solution. Ammonium paratungstate (APT) also could be produced from tungstic acid using by aqueous ammonium solution. The morphologies (cubic and plate types) of APT was controlled by the stirring process of purified solution of ammonium paratungstate.

Keywords: Raw material, Recycling, Ammonium paratungstate, Tungsten scraps, Extraction

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]. The wet treatments to recover tungsten and cobalt resources from tungsten scraps are high-cost processes and, at the same time, have very long processing time.

The general recycling process of tungsten scraps to produce tungsten raw materials (tungstic acid, ammonium paratungstate (APT) and WO_3) is carried out by the oxidation, milling, fusion, dissolution and extraction processes [6]. Among these steps, oxidation is the most important in determining the recovery rate of tungsten scraps. Therefore, the oxidation behavior of tungsten scraps should be investigated to achieve rapid and complete oxidation of the tungsten scraps.

Many studies on the high temperature oxidation of tungsten scraps have also been investigated in various aspects such as swelling kinetics, fracture resistance, and the effect of alloying composition [7-9]. However, they did not consider the possible effect of the rotary kiln with oxygen burner to accelerate the oxidation rate of scraps during the oxidation process. We investigated the oxidation behavior of tungsten scraps in the rotary kiln with oxygen burner.

In general, oxidized products is fused with sodium carbonate or sodium hydroxide to produce Na_2WO_4 in the general oxidation recycling process. And then the solid Na_2WO_4 is dissolved in the water [10]. This process takes very long reaction time and is high cost process. Therefore, we tried to increase the solubility of solid oxidized products to produce the solution of Na_2WO_4 by the hydrothermal reflux method [11]. And solution of Na_2WO_4 was used to produce $CaWO_4$ and H_2WO_4 by general chemical reactions with calcium chloride and hydrochloric acid [11]. Also to produce APT, ammonia solution was added to the tungstic acid. In this study, the extraction factor for morphologies (cubic and plate types) of APT was investigated by the stirring factor in the extraction process of purified solution of ammonium paratungstate.

2. Experimental

Tungsten scrap samples in a rod type, as shown in Fig. 1(a), were provided from an industry when they became useless for micro drill after sufficient usage. The average diameter of the sample fragments was about 3 mm and length is various (20-60 mm). The chemical composition of the tungsten scrap is 5% of cobalt, less than 0.5% of V-Cr-C, and 94.5% of tungsten carbide. Tungsten carbide, cobalt and V-Cr carbide phases were identified in XRD pattern, as shown in Fig. 1(b).

Fig. 2 shows the rotary kiln equipped with oxygen burner (SungJu Eng., Korea). The kiln temperature and oxygen gas contents in the kiln were analyzed by the gas analyzer (GreenLine MK2, Italy). The output of the oxygen burner could be adjusted by the ration of liquefied petroleum gas (LPG) and oxygen gas contents. The mixing ration of LPG and oxygen

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gas was 4-5 to 1. The kiln temperature was increased with increasing the output of oxygen burner. After reaching the temperature of 900° for 1hr, which the output of oxygen burner was 5%, average oxygen gas content in the kiln was 28%. When the output of oxygen burner was raised to 12%, the temperature of kiln was about 1010°. During the output of oxygen burner was increased by 12%, the oxygen gas content was increased to 40%. In this study, 100kg of tungsten scraps was set in the kiln. Kiln was rotated for 10s (2 rpm) at intervals of 5min. Scraps was oxidized in the kiln for 30, 60, 100, 120min. Oxidation rate of tungsten scraps was calculated by the residual scraps.

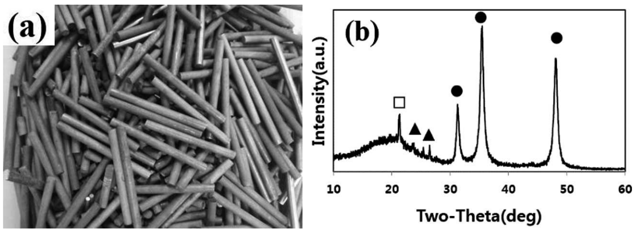

Fig. 1. Tungsten scrap samples in a rod type (a) and XRD pattern of scraps (b)

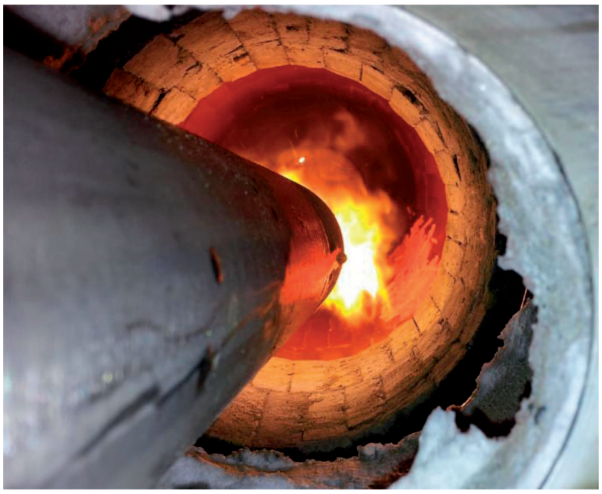

Fig. 2. Rotary kiln equipped with oxygen burner

Oxidized products of tungsten scraps was set in the hydrothermal reflux device (PolynanoTech, Korea) to dissolve and increase the solubility of solid oxidized products of tungsten scraps. In the hydrothermal reflux method, the cooling line in the hydrothermal reactor was adapted to decrease the pressure of reactor. This cooling (reflux) system increased the solubility of solid oxidized products. And 1kg of oxidized products was set in the hydrothermal reflux vessel and heated up at 150° and kept for 2hrs.

1mole% of calcium chloride solution was added in the solution of sodium tungsten oxide to precipitate $CaWO_4$. And the hydrochloric acid was added in the $CaWO_4$ to make tungstic acid. Finally an ammonia solution was added in the tungstic acid to make a pure APT. To extract the solid APT, clear solution of APT was boiled and then concentrated. During concentration process, stirring speed of solution was controlled.

The appearance of oxidized products was examined using optical microscope images and their microstructures were viewed using a scanning electron microscope (JSM-6390, JEOL). Chemical composition in specific regions of samples determined using an energy dispersive X-ray spectroscopy (EDS) system on the SEM. Tungsten scraps and oxidized products were identified using an X-ray diffractometer (XRD, D-max 2500poc, Rigaku) with Cu Kα radiation.

3. Results and discussion

Tungsten scraps were oxidized in the rotary kiln at 900° for 30, 60, 100, 120min. Oxidation rate of tungsten scraps was shown in Fig. 3. After 60min, the oxidation rate of scraps was 39%. Under the same conditions, after 120 min, the oxidation rate was 100%. If the rotary kiln was not rotated, the fully oxidized time of scraps become longer above 10hrs. However in this oxidation process of rotary kiln, scraps was fully oxidized just for 2hrs. The rotation of kiln causes the collision of scraps. The collision of scraps remove oxidized layer of scraps. Also the use of oxygen burner increases the oxygen gas contents in the kiln at high temperature. So that increased oxygen gas contents accelerate the oxidation of scraps. So these two factors accelerate the oxidation rate of scraps.

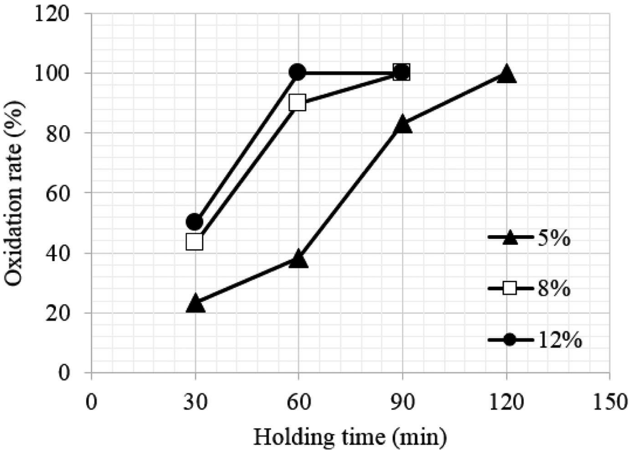

Fig. 3. Oxidation rate of tungsten scraps after oxidation process in the rotary kiln with oxygen burner

In classical dissolution process, it takes very long time to dissolve Na_2WO_4 [10]. To increase the solubility of solid oxide product, the hydrothermal reflux method was adapted. And 1mole of oxidized product ($CoWO_4$) was set in the reaction vessel with the NaOH solution. Three kind concentrations of NaOH solution, 0.1, 1.0, 10.0mole% were prepared. And each vessel was heated up 150° for 2hrs.

TABLE 1

Dissolution rate of oxide products by hydrothermal reflux process

Contents	Sample A	Sample B	Sample C
Concentrations	0.1M	1.0M	10.0M
Weight of oxide products	600g	600g	600g
pH	14	14	14
Dissolution rate	35%	63%	93%

The dissolution rate of sample C was increased to about 93% in the hydrothermal system. If oxidized product was dissolved in warm water, the dissolution rate was not so high.

However in this system, oxidized product ($CoWO_4$) was fully dissolved just for 2hrs in the hydrothermal reflux system. After sedimentation process, aqueous sodium tungstate was separated from Co-Cr-V oxide by-product. In order to extract the tungstic acid from aqueous sodium tungstate proceeded as follows.

$$Na_2WO_4 + CaCl_2 \longrightarrow CaWO_4 + 2NaCl \qquad (1)$$

$$CaWO_4 + 2HCl \longrightarrow H_2WO_4 + 2CaCl_2 \qquad (2)$$

When 1mole of calcium chloride solution was added to a sodium tungstate solution until pH value reached at neutral, white crystal of calcium tungsten oxide was precipitated. After sedimentation time, solid calcium tungsten oxide was separated from solution and washed several times. To get a tungstic acid from calcium tungsten oxide, hydrochloric acid (d:1.16) was added to calcium tungsten oxide and stirred for 2hrs. And then to increase the oxidation of tungstic acid, a small amount of nitric acid (d:1.35) was added. Finally yellow crystal of tungsten acid was precipitated. Also after sedimentation, solid crystal of tungstic acid was separated from solution and washed several times.

The crystallization process of APT can be expressed as follows [12]:

$$10NH_4^+ + H_2W_{12}O_{42}^{-10} + xH_2O \rightarrow (NH_4)10H_2W_{12}O_{42} \cdot xH_2O) \qquad (3)$$

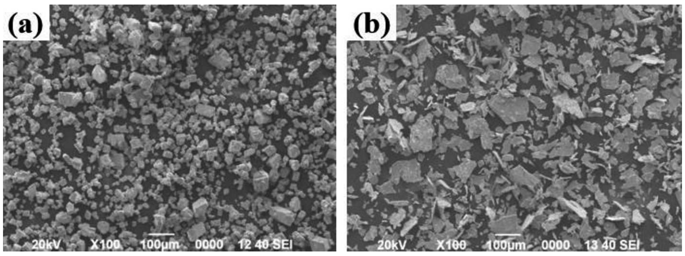

Fig. 4. Microstructure of APT crystals (a) cubic type and (b) plate type

To form the ammonium paratungstate, the ammonia solution (d:0.9) was added to the tungstic acid. As pH value of tungstic acid reached at neutral, APT suspension was first generated. If more ammonia solution was added, the transparent APT solution was obtained. To extract the solid APT, the clear solution of APT was boiled and then concentrated. The stirring effect in the concentration process was investigated. During concentration process, white APT crystals was precipitated. Fig. 4(a) shows cubic type of APT crystal. This samples was stirred at 300rpm in the concentration process. But if the solution of APT was not stirred in the concentration process, plate type of APT was precipitated, as shown in the Fig. 4(b). These two APT samples were identified through the SEM and XRD patterns. A high purity APT could be prepared by the concentration crystallization process and quantitative analyses of APT was carried out by ICP-OES instrument (PerkinElmer 5300 DV). In the results of chemical analysis of APT powder, major metal impurities in APT are silicone (210 ppm), Ta (310 ppm), Nb (303 ppm), V (98 ppm), Mo (51ppm) and the purity of APT is found to be 99.9%.

4. Conclusions

Oxidation rate of tungsten scraps and solubility of oxide products of scraps were promoted by the rotary kiln with oxygen burner and the hydrothermal reflux method, respectively. By heating tungsten scraps in rotary kiln with oxygen burner at around 900° for 2hrs, the scraps was oxidized completely. Then oxidized products (WO_3 and $CoWO_4$) were fully dissolved in the solution of NaOH by hydrothermal reflux method at 150° for 2hrs. The dissolution rate was increased with increasing the reaction temperature and concentration of NaOH. And then $CaWO_4$ and H_2WO_4 could be generated from the aqueous sodium tungstate solution. Ammonium paratungstate (APT) also could be produced from tungstic acid using by aqueous ammonium solution. The morphologies (cubic and plate types) of APT was controlled by the stirring process of purified solution of ammonium paratungstate.

Acknowledgements

This work was supported by Inter-ER Cooperation Projects under the Ministry of Trade, Industry and Energy, Republic of Korea.

REFERENCES

[1] S. Hong, J. Song, S. Lee, H. Hong, H. Kang, J. Kor. Powd. Metall. Inst. **19**, 79 (2012).
[2] S. Venkateswaran, W.D. Schubert, B. Lux, M. Ostermann, B. Kieffer, Int. J. Refract. Met. H. **14**, 263 (1996).
[3] J.C. Lin, J.Y. Lin, S.P. Jou, Hydrometallurgy **43**, 47 (1996).
[4] C. Edtmaier, R. Schiesser, C. Meissl, W.D. Schubert, A. Bock, A. Schoen, B. Zeiler, Hydrometallurgy **76**, 63 (2005).
[5] T. Kojima, T. Shimizu, R. Sasai, H. Itoh, J. Mater. Sci. **40**, 5167 (2005).
[6] G.G. Lee, H.S. Kwon, G.H. Ha, J. Kor. Powd. Metall. Inst. **11**, 111 (2004).
[7] F. Lofaj, Y. Kaganovskii, J. Mater. Sci. **30**, 1811 (1995).
[8] B. Casas, X. Ramis, M. Anglada, J.M. Salla, L. Llanes, Int. J. Refract. Met. H. **19**, 303 (2001).
[9] V.B. Voitovich, V.V. Sverdel, R.F. Voitovich, E.I. Golovko, Int. J. Refract. Met. H. **14**, 289 (1996).
[10] E. Lassner, Int. J. Refract. Met. H. **13**, 35 (1995).
[11] J.C. Lee, E.Y. Kim, J.H. Kim, W.B. Kim, B.-S. Kim, B.D. Pandey, Int. J. Refract. Met. H. **29**, 365 (2011).
[12] W.V. John, Int. J. Refract. Met. H. **13**, 61 (1995).

Received: 20 November 2014.