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Reduction of WO_3 to W-metal by mechanochemical reaction

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ABSTRACT

A new non-thermal route for reduction of tungsten oxide (WO_3) to metallic tungsten (W) by a milling operation in ammonia (NH_3) gas atmosphere in the presence of lithium nitride (Li_3N) is proposed in this paper. A sample of WO_3 was milled with Li_3N under ammonia gas atmosphere in a planetary ball mill with ZrO_2 balls to induce mechanochemical (MC) reaction between the starting samples. Characterization of milled product by X-ray diffraction (XRD) analysis confirms that W-metal could be obtained by the new mechanochemical (MC) process within 1 h.

1. Introduction

Tungsten (W) is a rare metal, and with its unique properties such as high melting point (3422 °C), excellent high-temperature mechanical properties, high thermal and electrical conductivities, high hardness, is used in a wide variety of commercial and industrial uses as tungsten carbide, as alloy additive, as pure tungsten, and as tungsten chemicals [1–3]. The chief economic minerals of tungsten are wolframite ($(Fe,Mn)WO_4$)) and sheelite ($CaWO_4$) and extraction of W-metal from those minerals is achieved through high temperature and pressure processes followed by alkaline solution leaching [2,3].

The grade of tungsten containing scrap was reported to be in the range (40–95 wt.% W) as compared high grade raw material containing (7–60 wt.% W) and about one-third of total demand for tungsten in the world is supplied from scrap [2,4]. Recovery of W-metal from scrap containing tungsten by alkaline solution/leaching process for useful industrial application is discussed elsewhere [4,5]. Recovery of tungsten as WO_3 from tungsten catalysts in a reaction system containing an organic compound and hydrogen peroxide was reported [6]. These methods require high temperature/pressure, acid and/or basic solutions involving several operational steps.

Application of mechanochemical effect by a milling operation to induce mechanochemical effects such as phase transformation and solid state reaction is widely available in literature [7–13]. A process involving milling to effect MC reaction between $CaWO_4$ and magnesium to obtain W-metal is also reported [14,15]. In this work we have developed a new process involving MC reaction between WO_3 and Li_3N under NH_3 gas to obtain W-metal.

2. Experimental

2.1. Sample preparation and MC reaction

Tungsten oxide (WO_3) and lithium nitride (Li_3N), supplied by Wako Pure Chemical Industries, Ltd., Japan, were used as starting materials. A planetary ball mill (P-7, Fritsch, Germany), having a pair of ZrO_2 mill pots charged with 24 × 10 mm balls in each pot, was used for the milling of WO_3 with Li_3N in NH_3 gas atmosphere. The inner diameter and length of the mill pots are the same size (40 mm).

A sample mixture of 2.9 g WO_3 (2.0 g) and Li_3N (0.9 g) for a molar ratio of ($1:3 = WO_3:Li_3N$) was charged into the mill pot and then the mill pot was set in a container made of stainless steel (overpot) as shown in Fig. 1. The inner air in the mill pots was degassed with a vacuum pump, and charged with NH_3 gas at 0.8 MPa. The mill pots were set at the mill device to run at 300 rpm for different times. The milled product was removed from the pots and washed in water for 10 min to remove soluble by-products and to recover W-metal. Overall schematic illustration of the experimental procedure is shown in Fig. 2.

2.2. Characterization

X-ray powder diffraction (XRD) analysis using Rigaku, RINT-2200/PC system with a Cu Kα irradiation source ($\lambda = 1.5405$ Å) at 40 kV and 20 mA in a continuous scan mode between 10 and 60° in 2θ was used to analyze solid products after milling. Morphology of the milled mixture was observed by Scanning Electron Microscope (SEM) equipment, S-4100L (Hitachi).

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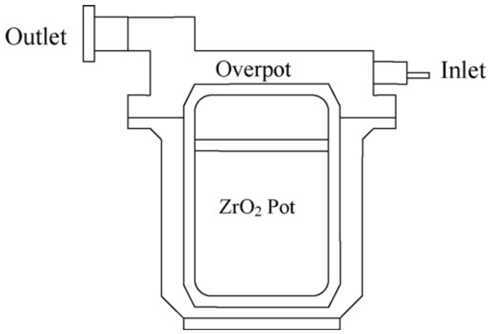

Fig. 1. Illustration of ZrO_2 pot covered with stainless steel pot.

3. Results and discussion

3.1. Mechanochemical (MC) reaction

A sample mixture of WO_3/Li_3N (1:3) milled in NH_3 gas environment for 1 h to effect MC reaction between the starting materials to reduce WO_3 to W-metal is shown in Fig. 3 (XRD patterns). It could be seen from the figure that, peaks of WO_3 sample before milling (a) were completely removed as a result of MC reaction and new dominant peaks of W-metal appear in the milled product (b). Washing milled product in water for 10 min allowed removal of water soluble compounds such as $LiOH{\cdot}H_2O$ formed during MC reaction leading to recovery of pure W-metal (Fig. 3(c)). The overall mechanochemically induced solid state reaction when WO_3 is milled with Li_3N under NH_3 gas environment could be represented by the reaction, Eq. (1):

$$WO_3 + Li_3N + NH_3 \rightarrow W + 3LiOH + N_2 \qquad (1)$$

$$WO_3 + 2Li_3N \rightarrow W + 3Li_2O + N_2 \qquad (2)$$

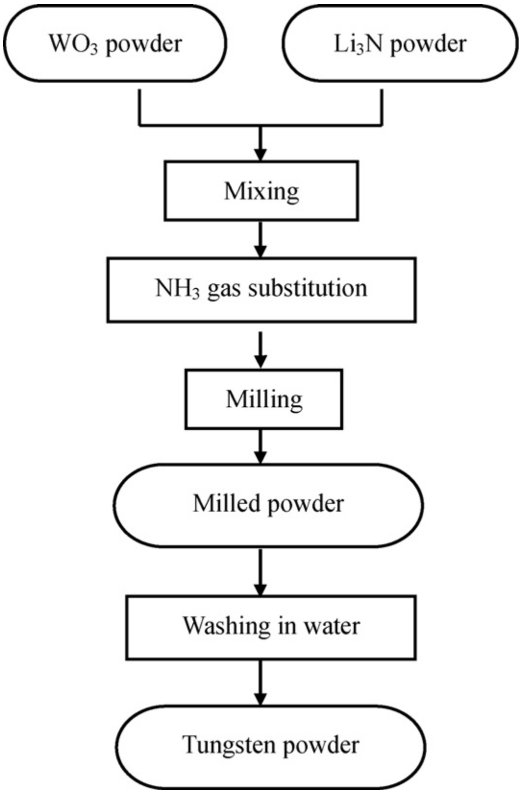

Fig. 2. Schematic illustration of the experimental procedure used to effect mechanochemical reduction of WO_3.

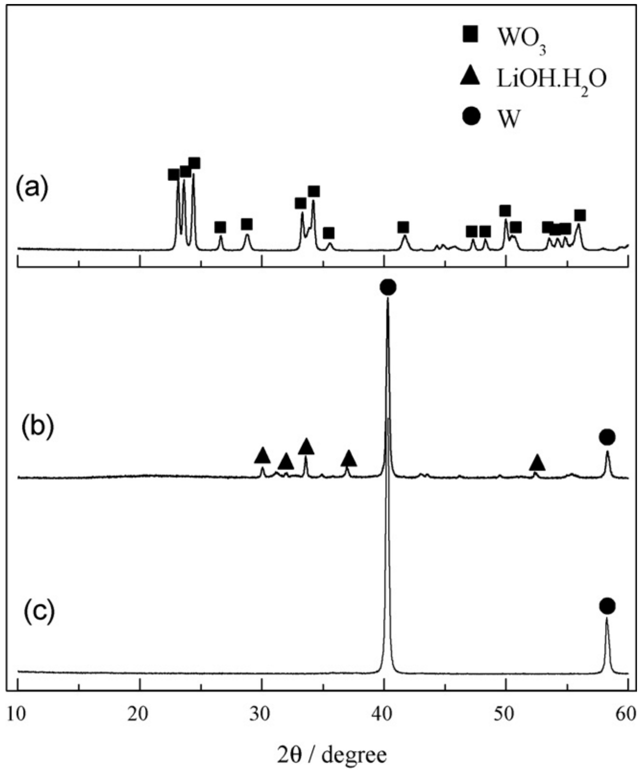

Fig. 3. XRD patterns of (a) WO_3 sample before milling, (b) WO_3/Li_3N (1:3, mol/mol) sample mixture after milling in NH_3 gas environment for 1 h and (c) after washing milled sample in (b) with water.

From our previous experience [11–13], gaseous reagents such as NH_3 and N_2 do not clearly enter in reaction; however, they could create a reducing or non-oxidative environment which assists the rate of reductive reaction. In order to investigate the reaction mechanism between WO_3 and Li_3N under NH_3 gas environment, a

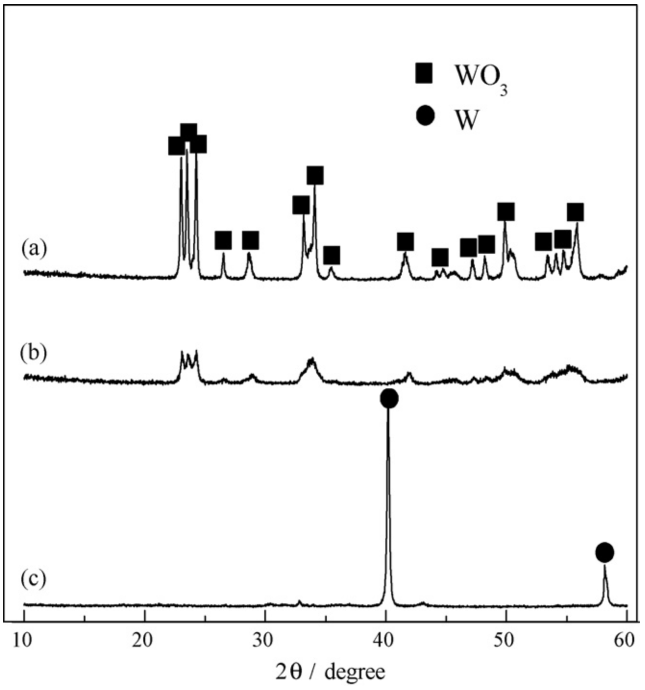

Fig. 4. X-ray diffraction patterns of (a) WO_3 sample before milling, (b) WO_3 sample milled in NH_3 gas environment for 1 h and (c) WO_3/Li_3N (1:3) mixture milled in N_2 gas environment for 1 h.

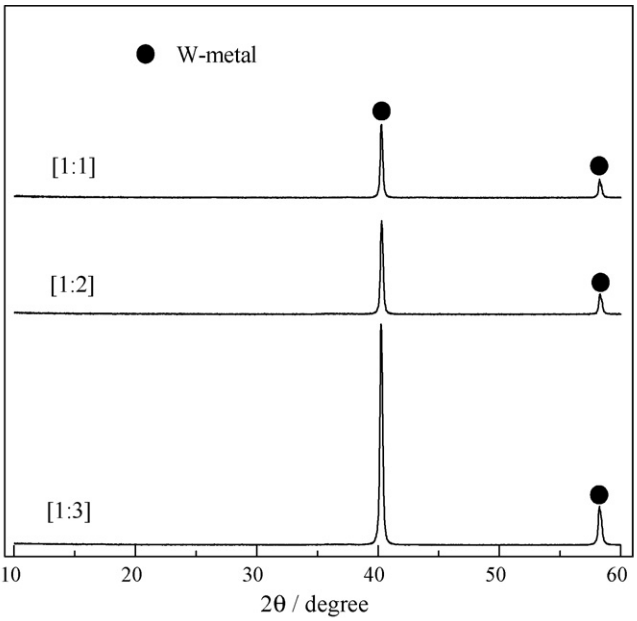

Fig. 5. XRD patterns of WO_3/Li_3N sample mixture of varying molar ratios milled in NH_3 gas environment for 1 h at 300 rpm and washed in water for 10 min.

sample of WO_3 was milled first without Li_3N but under NH_3 gas environment and another sample of WO_3 was milled with Li_3N under N_2 gas environment. Fig. 4 shows X-ray diffraction patterns of (a) WO_3 before milling, (b) WO_3 milled in NH_3 gas environment for 1 h, and (c) WO_3/Li_3N (1:3) mixture milled in N_2 gas environment for 1 h. The figure clearly shows that milling of WO_3 without Li_3N only shows a reduction of peak intensity as sample is transformed to amorphous phase due to the milling impact, even in the presence of NH_3. Milling of WO_3 with Li_3N under N_2 gas environment gives results similar to NH_3 and the likely reaction between WO_3 and Li_3N can be represented by the reaction Eq. (2). All preceding tests were conducted under NH_3 gas environment.

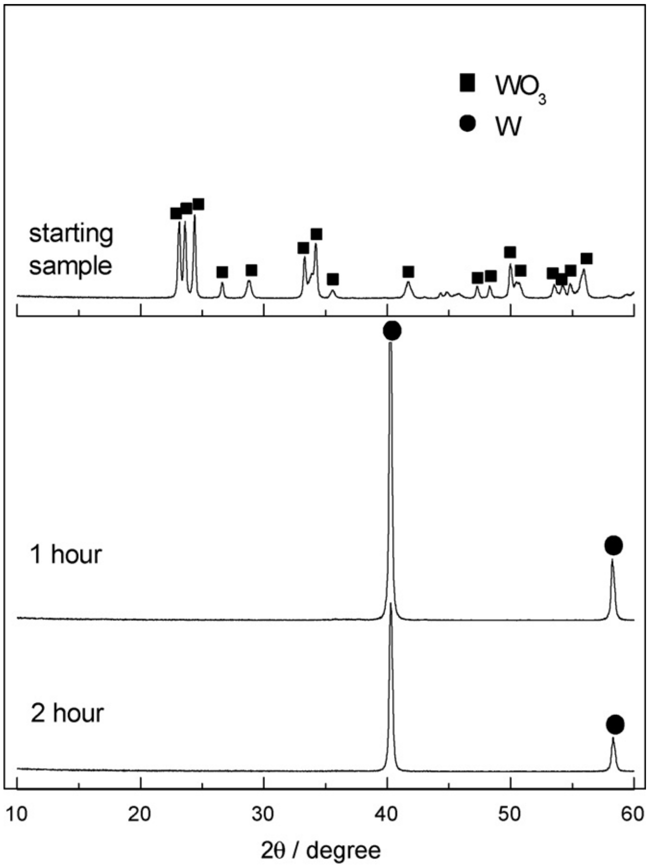

Fig. 6. XRD patterns of WO_3/Li_3N (1:3) sample mixtures milled in NH_3 gas environment for different milling times and washed in water.

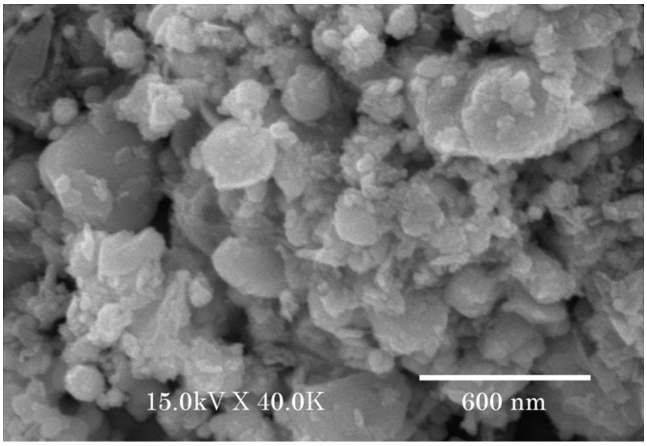

Fig. 7. SEM image of WO_3/Li_3N (1:3) sample mixture milled in NH_3 gas atmosphere for 1 h at 300 rpm.

Reaction under NH_3 gas environment as given in Eq. (1) suggests that 1 mol of each of the starting materials (WO_3, Li_3N and NH_3) is required to obtain W-metal. However, to increase reaction rate for WO_3 reduction to W-metal, excess amount of Li_3N would be required to induce MC reaction between starting materials during milling. Fig. 5 shows effect of Li_3N addition from 1 to 3 mol (1:1, 1:2 and 1:3 = WO_3:Li_3N) and NH_3 moles constant at 1.9 mol (0.8 MPa). The peak intensity of W-metal is similar at (1:1) and (1:2), however, the peak intensity is twice stronger when Li_3N addition is increased to (1:3).

A sample mixture of WO_3/Li_3N (1:3) was milled for 1 and 2 h respectively to investigate effect of reaction time and results obtained is shown in Fig. 6. The peak intensity of sample mixture milled for 1 h is twice stronger (Fig. 6(a)), than sample mixture milled for 2 h (Fig. 6(b)). This suggests that MC reaction between the starting materials is completed within 1 h of milling, and further milling changes W-metal formed to amorphous phase.

Fig. 7 shows the SEM image of WO_3/Li_3N (1:3) sample milled for 1 h under NH_3 gas atmosphere and washed in water for 10 min. W-metal of sub-micron size resulting from milling operation and MC reaction could be seen from the SEM image.

4. Conclusion

A new non-thermal process for the reduction of WO_3 to W-metal was developed in this work. In the new process, a mixture of WO_3 and Li_3N under NH_3 or N_2 atmosphere was subject to milling in a planetary ball mill to effect MC reaction between the starting materials. Characterization of the milled products by XRD showed W-metal as the single dominant phase and subsequent washing of milled products after milling results in removal of soluble $LiOH{\cdot}H_2O$ leading to recovery of high purity W-metal. The results showed that W-metal could be obtained by this process within 1 h of milling WO_3/Li_3N (1:3) mixture at a moderate mill speed of 300 rpm, followed by washing in water for 10 min. The result also shows that a non-oxidative environment, as in this case provided by NH_3 or N_2 gases allows the reductive reaction between WO_3 and Li_3N to proceed fast to completion at faster rate.

This process could be applied to recovery of W-metal from tungsten bearing wastes, as it avoids high temperature, acidic solution, and many operational steps.

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