Influence of partial pressure of water vapor on anodic dissolution of tungsten from super hard alloy tools in molten sodium hydroxide

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ABSTRACT

As part of an ongoing study of a new tungsten recycling process using a molten sodium hydroxide bath, in which tungsten is anodically dissolved in the melt from tungsten-containing secondary resources, the influence of the partial pressure of water vapor on the electrochemical behavior of tungsten, cobalt, nickel, and tungsten carbide was investigated. Cyclic voltammograms of cobalt suggested that the solubility of cobalt compounds increased with the partial pressure of water vapor, whereas tungsten and tungsten carbide underwent no significant changes during their oxidation step. In addition, the current attributable to the evolution of hydrogen gas was measured when the partial pressure of water vapor became higher than 0.5 atm. On the basis of the above-mentioned results, anodic dissolution was carried out at a constant cell voltage using a super hard alloy tool. When water vapor was introduced into the system, the cell voltage and period required to dissolve the entire tip were reduced, even though the applied cell voltage was less than half that required under a pure argon atmosphere. These results indicate that the introduction of water vapor has the potential to improve the anodic dissolution step in the tungsten recycling process using a molten sodium hydroxide bath.

1. Introduction

Tungsten (W) is widely used in industries owing to its high hardness, melting point, density, and so on. At least 60% of the W consumed in Japan and the US is used in cemented carbide or super hard alloy [1,2], which is mainly used in machining industries and is composed of tungsten carbide (WC) and binder metals such as cobalt (Co) and nickel (Ni). Mineral sources of W, however, are relatively scarce. Thus, the recycling of W is one of the most important methods of utilizing the limited resources effectively.

Waste super hard alloy can be categorized into "hard" and "soft" scrap, which represent solid pieces and sludges, respectively. From soft scrap, W is commonly recovered via the following steps, as shown in Fig. 1a: a) W-containing scrap is roasted in air in order to oxidize WC to tungsten oxide; b) the tungsten oxide formed is dissolved in an aqueous sodium hydroxide (NaOH) solution; c) W is purified via hydrometallurgical processes such as ion exchange, pH control, precipitation, and solvent extraction; and d) W is recovered in the form of ammonium paratungstate (APT) by crystallization from an ammoniacal solution [3]. APT obtained in this way is recognized as an important intermediate product, and W or WC particles are produced from this material by reduction using hydrogen (H₂) gas, carbonization, and so on.

The abovementioned conventional process is well-established and has advantages in the purity of the W obtained, which is comparable to that of W obtained from ores. On the other hand, the application of this process to hard scrap is difficult and requires either long-term roasting, for example, 48 h at 1098 K [4], or the repetition of the roasting step a) and the dissolution step b), because of the difficulty in oxidizing entire pieces at once.

From this background, some processes have been proposed in order to establish an appropriate method for recycling hard scrap using aqueous solutions [5–8] or molten salts [1,9–11]. The latter method mainly employs molten sodium nitrate (NaNO₃) or sodium nitrite (NaNO₂) as a reagent for oxidizing WC and a reaction medium, and W-containing alkaline solutions are obtained by dissolving the solidified melt, as shown in Fig. 1b [1,9]. Although the reactivity of molten NaNO₃ and NaNO₂ with WC is sufficient, it is very difficult to control. In addition, some equipment for neutralizing NOₓ gas, which is generated as a result of the reduction of NaNO₃ and NaNO₂, is required. In order to carry out the oxidation of WC under more moderate conditions, molten Na₂SO₄ and Na₂SO₄-NaOH systems have also been examined [10,11]. In these systems, however, SOₓ gas is generated instead of NOₓ gas, and high temperatures of 1100 K or more are required owing to the low reactivity. Recently, the present authors have proposed another

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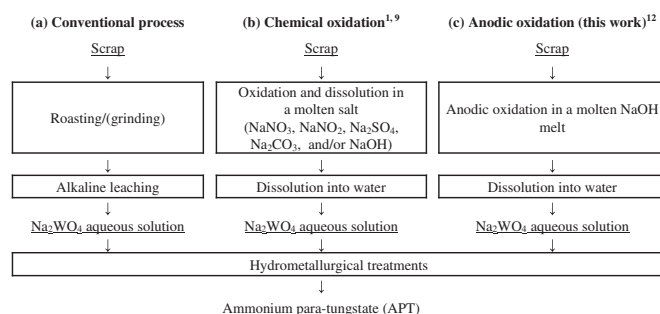 *E-mail address:* tetsuo.oishi@aist.go.jp (T. Oishi).

Fig. 1. Flow sheet of tungsten recycling processes: (a) conventional process mainly used for soft scrap, (b) chemical oxidation by a molten salt or air, and (c) anodic oxidation in an NaOH melt, as proposed by the authors (reprinted and modified from our previous paper [12]).

process using anodic dissolution in molten NaOH [12,13]. In this process, a super hard alloy tool as a model sample of hard scrap is used as the anode, and all the WC and Co, which is used as a binder metal, are dissolved in the melt. Dissolved W ions remain in the molten NaOH bath, and a solution of sodium tungstate-NaOH is obtained by dissolving the solidified melt in water. The aqueous solution obtained in this way is basically the same as that obtained in the conventional process for recycling soft scrap mentioned above, and W could be recovered via hydrometallurgical and reduction steps. In addition, most of the dissolved Co in the melt is deposited on the cathode as Co metal particles. Thus, Co could also be recovered in this process. Similar results were reported by other researchers, although they claimed that Co was not dissolved from the anode [14].

On the other hand, it was recognized that the water vapor pressure has a significant influence on a variety of reactions in molten alkali metal hydroxide systems [15,16]. Thus, the present study focused on the influence of the water vapor pressure on the anodic dissolution of W and other metals in order to obtain a better insight into the present system and to improve the electrochemical recycling of W using molten NaOH.

2. Experimental

A schematic drawing of the experimental apparatus is shown in Fig. 2. A total of 40 g NaOH (Wako Pure Chemical Co., Ltd) was placed in a glassy carbon crucible (i.d. 40 mm, height 40 mm) and fused at
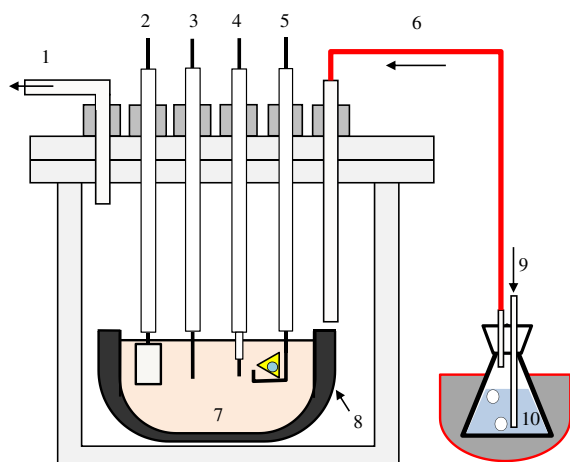

Fig. 2. Schematic drawing of the experimental apparatus. 1: Ar gas and water vapor outlet. 2: Counter electrode (Ni plate). 3: Quasi-reference electrode (W wire). 4: Working electrode for cyclic voltammetry (Ni, Co, W wire). 5: Working electrode for electrolysis at a fixed cell voltage (throw-away tip on a Ni plate). 6: Flexible stainless tube with heaters and gas inlet. 7: NaOH melt at 723 K. 8: Glassy carbon crucible. 9: Ar gas inlet. 10: Water bath in a mantle heater.

723 K. The partial pressure of water vapor was controlled by passing argon (Ar) gas through a water bath kept at 294–363 K and introducing water vapor containing Ar gas into the reaction chamber. Before the measurements, this gas mixture was bubbled into the melt for more than 2 h. Strictly speaking, this period was insufficient to enable equilibrium between the water in the melt and the water vapor in the gas phase to be reached. However, the difference in the water content between the present and the equilibrium conditions was less than 10%, and its impact on the results of cyclic voltammetry was found to be negligible in the present study.

2.1. Cyclic voltammetry

The working electrode used was either an Ni wire ($\varphi = 1$ mm), a Co wire ($\varphi = 1$ mm), or a W wire ($\varphi = 1$ mm). Although the exact surface area was difficult to measure, a pellet of WC ($\varphi = 1$ mm and length = 5 mm) held by an Ni wire was also used as the working electrode in order to observe the electrochemical behavior of WC. The counter electrode was an Ni plate (10 mm × 20 mm), and a W wire ($\varphi = 1$ mm) was used as a quasi-reference electrode. The voltammetry was continued for three or more cycles, and the results of the last cycle were used in this study.

2.2. Electrolysis at a fixed cell voltage

A commercially available throw-away tip with no coating (surface area of approximately 2 cm^2) was used as a model sample of hard scrap. As shown in Fig. 2, the tip was placed on an Ni plate and used as the anode. The edge of the Ni plate was turned up in order to prevent WC particles from dropping from the Ni plate. An Ni plate of dimensions of 10 mm × 20 mm was used as the cathode. Electrolysis was conducted at a fixed cell voltage because of the unstable potential of the quasi-reference electrode. The cell voltage applied was selected in order to pass nearly the same current as that observed in the absence of water vapor in our previous work, which was approximately 0.15 A in the initial stage of electrolysis [12]. This current corresponded approximately to a current density of 0.07 A/cm^2 on the tip. Electrolysis was terminated when the passed current became of the same order as the residual current.

3. Results and discussion

3.1. Cyclic voltammetry at various partial pressures of water vapor

Cyclic voltammograms for the Ni electrode are shown in Fig. 3a. When the partial pressure of water vapor was 0.08 atm, an anodic current peak due to the formation of a passive film was observed at a potential of 0.5 V during the anodic scan. The current observed above 1.2 V is attributable to the evolution of oxygen gas. During the cathodic scan after the formation of the passive film, a corresponding cathodic current was observed from 0.3 to − 0.2 V. In the potential region below − 0.5 V, a cathodic current due to the electrodeposition of sodium (Na) was observed:

$$Na^+ + e \Rightarrow Na \tag{1}$$
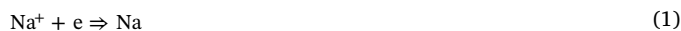
When the partial pressure of water vapor increased to 0.5 atm or greater, a new cathodic current was observed in the potential region below − 0.1 V, and this current increased with the partial pressure of water vapor. Thus, the observed current is attributable to the reduction of water and probably the evolution of H$_2$ gas:

$$H_2O + e^- \Rightarrow 1/2\,H_2 + OH^- \tag{2}$$

The characteristic potential–current profile observed in this potential region could be explained by a change in the surface conditions of the Ni electrode. In other words, the generation of H$_2$ gas started at − 0.1 V, and the reaction ratio increased during the potential sweep in