Recycling of Tungsten by Molten Salt Process

Tetsuo Oishi

Abstract Tungsten (W) is one of the most important metals in various industries, particularly in the machining industry. At least 60% of W is consumed in cemented carbide or super-hard alloys in Japan and the USA. The major recycling method for cemented carbides is the hydrometallurgical process combined with the roasting step, which oxidizes W in scrap into tungsten oxide. However, this conventional process requires repetition of roasting and dissolution in some cases, which makes the process costly and inefficient. In contrast, the molten salt process has specific advantages in terms of processing rate and simplicity. In this study, the recycling processes for W using molten salt are reviewed. Subsequently, our new recycling process using molten hydroxide is introduced, and recent data on this process discussed.

Keywords Rare earth elements · Recycling · Molten salt electrolysis · Alloy diaphragm

Introduction

Tungsten (W) is widely used in industries owing to its high hardness, melting point, and density. According to the literature, more than 60% of W is consumed in cemented carbide or super-hard alloys in Japan and the USA [1, 2]. Super-hard alloys are mainly used in machining industries and are composed of tungsten carbide (WC) and binder metals such as cobalt (Co) and nickel (Ni), as shown in Fig. 1. However, mineral sources of W are relatively scarce and unevenly distributed in the Earth's crust. Thus, the establishment of efficient W-recycling processes is one of the most important objectives for effectively utilizing the limited W resources.

Recycling processes for super-hard alloys are generally categorized into direct and indirect methods (Fig. 2) [3]. In the direct method, zinc (Zn) treatment is typically employed to make super-hard alloy scraps easy to crush in which cracks are

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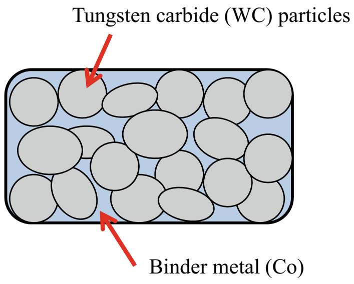

Fig. 1 Schematic drawing of cemented carbide (super hard alloy)

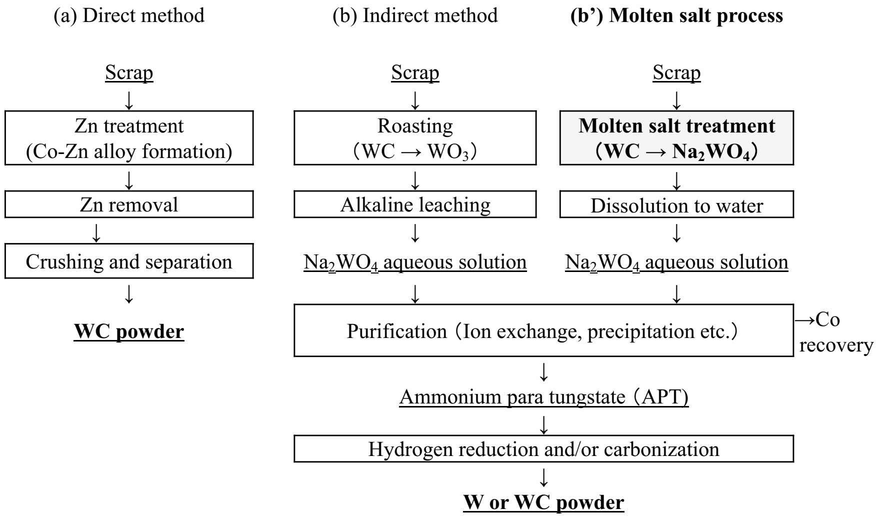

Fig. 2 Flow of typical direct and indirect methods

formed during the Zn–Co alloy formation step. After the evaporation of Zn from the Zn–Co alloy, the super-hard alloys are easily crushed, and WC powder is recovered via conventional physical separation steps. Although this method is simple and inexpensive, the use of recovered WC powder is limited because it essentially has no purification effect. The indirect method is also known as the chemical method. The super-hard alloy scrap is typically roasted in air to oxidize WC to WO_3. Thereafter, the roasted scraps are dipped in NaOH solutions, and W is dissolved. After purification of the NaOH solutions, W is recovered as ammonium paratungstate (APT), which is an important intermediate product from W ore during W metallurgy. WC and/or W powder are commonly produced from APT by roasting, hydrogen reduction, and carbonization. The indirect method has a high purification effect and is applicable to various super-hard alloy scraps; however, this method requires repetition of roasting and dissolution in some cases, which makes the process costly and inefficient.

Several other processes have been proposed and investigated from the past to date. Because numerous review papers have already been published on the W-recycling process [4–9], this paper focuses on the molten salt process proposed and/or investigated for W-recycling. The molten salt process has specific advantages in terms of processing rate and simplicity. First, some molten salt processes available in the literature were reviewed. Subsequently, our new recycling process using molten hydroxide was introduced, and the recent progress in this process discussed.

Molten Salt Processes from the Past to Date

Molten salt processes are mainly categorized as indirect methods. The conventional indirect method has an operational problem in that it is difficult to oxidize the entire scrap simultaneously when the method is applied to relatively large objects. This complicates the process by requiring repeated operations, such as roasting, alkali leaching, or peeling of the surface layer. The molten salt process is a solution to this problem (Fig. 2b). In other words, the main subject of the molten salt processes is the efficient oxidation of WC and W to water-soluble W species such as WO_3 and Na_2WO_4.

Some of the molten salt processes available in the literature are summarized in Table 1. More than half of them are patent documents, and because of the nature of patents, they tend to be broadly described. For instance, when sodium chloride (NaCl) is considered, it is often referred to as "alkali metal chloride." In commercial applications, however, it is difficult to consider options other than sodium salt from a cost perspective. Thus, all of them are described as sodium salts rather than "alkali metal salt" in this paper. As already mentioned, it is important to efficiently oxidize WC and W in the molten salt process, and the description is differentiated by the oxidant used.

Table 1 Molten salt processes for W-recycling

Oxidizing agent	Dilutant	Operation Temperature	Characteristics	References
$NaNO_3$ or $NaNO_2$ (with support by O_2 in some cases)	Na_2CO_3	800 °C	Rapid reaction Difficult to control Generation of NO_x gas	[4, 6]
	NaOH (+ NaCl)	400 ~ 700 °C		[10, 13, 14]
	MCl (M = Li, Na, K)	400 ~ 700 °C		[15]
	No	700 ~ 900 °C		[11, 16, 17]
O_2	Na_2CO_3	800 ~ 1000 °C	Low reactivity	[18, 19]
Na_2SO_4	NaOH	800 ~ 1100 °C	Relatively low reactivity Generation of SO_x gas	[20]
	NaOH + MO (M = Co etc.)	900 ~ 1100 °C		[21]

Sodium nitrate ($NaNO_3$) and sodium nitrite ($NaNO_2$) are the most popular oxidizing agents in this field. In the report by Shedd, which summarizes the situation of tungsten recycling in the USA, only the process using $NaNO_3$ and $NaNO_2$ as oxidizing agents and sodium carbonate (Na_2CO_3) as a diluent is introduced [6]. According to a review by Bhosale et al. [10], $NaNO_3$ or a mixture of $NaNO_3$ and Na_2CO_3 is widely used in the field of W metallurgy, at least by 1990. The main reaction in the presence of oxygen is explained by the following equation [11]:

$$WC + 3NaNO_3 + 1/4O_2 \rightarrow Na_2WO_4 + 3NO + CO_2 + 1/2Na_2O \tag{1}$$

Fs patent (US-1652646, 1927) as a processing method to obtain Na_2WO_4 from ores [12]. Tungsten in ores exists in a hexavalent state such as $CaWO_4$ and (Fe, Mn)WO_4, which is different from the treatment of WC and W to be recycled. However, the use of $NaNO_3$ as an oxidizing agent for various tungsten ores has been observed in several patents related to tungsten smelting in the 1910s–1920s and is assumed to have been widely recognized in this field. Although the molten salt process using $NaNO_3$ has a disadvantage in that NO_x gas is generated and exhaust gas treatment is required, it is superior in that the reaction proceeds quickly because of the strong oxidizing nature of $NaNO_3$. However, according to Lassner, this is an extremely violent reaction and “difficult to control [4].” The same has been highlighted in several patent documents, and methods using NaOH or alkali metal chlorides as diluents have been proposed to address this problem [10, 13–15]. Among these methods, a system using NaOH as a diluent was introduced in detail by Bhosale et al. [10]. According to them, the reaction can be well controlled, and NO_x generation can be suppressed under appropriate conditions. It has also been reported that Sandvik Asia Ltd. has already started operations on a semi-commercial scale. The combination of molten NaOH and $NaNO_3$ is superior to other molten salt processes in that it can be operated at a relatively low temperature of approximately 450 °C, and it also suppresses the generation of NO_x gases. However, if the following process flow is similar to that shown in Fig. 2b, the diluent will be dissolved in water at a later stage. Thus, the chemical cost increased as the amount of diluent increased, although the control of the reaction rate became easier.

As an alternative approach, Ikegaya and co-workers succeeded in controlling the reaction by accurately controlling the feeding rate of $NaNO_3$ [11, 16]. Notably, they succeeded in controlling the reaction, which had been considered “difficult to control” for a long time, without using a diluent such as NaOH. In addition to the molten salt process, they invented an efficient hydrometallurgical process to remove impurities and developed an exhaust gas treatment facility for NO_x gas. This process has been commercialized after further investigation and improvement [17].

Although $NaNO_3$ is the major oxidizing reagent in this field, as mentioned, other oxidizing agents such as O_2 gas and sulfide ions have also been investigated. Scott proposed a process for oxidizing and extracting the tungsten component to obtain Na_2WO_4 by contacting W-containing scraps with molten Na_2CO_3 at 800–1000 °C in air [18]. Recently, Yasuda et al. proposed the oxidation and dissolution of W from super-hard alloy scraps in molten Na_2CO_3 under controlled O_2 and CO_2 partial pressures. Although this study is in the fundamental stage, they found that CO_3^{2-} ions can also be an oxidizing agent for metallic W in addition to O_2 gas under specific conditions [19]. Lohse proposed a method of blowing air into a mixture of molten NaOH and sodium sulfate (Na_2SO_4) [20]. The problem here is that it is difficult to obtain a sufficient reaction rate with oxygen and sulfate. Therefore, it is necessary to maintain the reaction chamber at a temperature of 900 °C or higher, resulting in high energy consumption and serious damage to the equipment. Compared to oxygen (or air), Na_2SO_4 seems to oxidize faster, but SO_x is generated when the sulfate is reduced; therefore, an exhaust gas treatment facility is required, as in the case of $NaNO_3$ [7]. Itakura et al. reported the formation of soluble sulfides such as sodium sulfide (Na_2S) as a further problem when Na_2SO_4 was used [21]. This may lead to the generation of hydrogen sulfide (H_2S) gas during the subsequent hydrometallurgical process, and elemental sulfur may precipitate, which decreases the purity of the recovered tungsten compound. However, the formation of water-soluble sulfides can be avoided by the addition of metal oxides to molten salts. In this case, Na_2S reacts with other metal oxides, and water-insoluble metal sulfide is obtained according to the following reaction, which can avoid one of the problems of the Na_2SO_4 process [21].

$$Na_2S + MO \rightarrow Na_2O + MS \tag{2}$$

where M is typically iron, cobalt, or nickel. Among these metals, cobalt (cobalt oxide or cobalt tungstate) is suitable because the use of Co compounds is effective not only in reducing the abovementioned water-soluble sulfides but also in avoiding complications of the subsequent purification process; that is, the insoluble sulfide can be separated as a precipitate when the processed molten salt is dissolved in water, and the main component of the precipitates obtained here is cobalt when super-hard alloy scrap is processed. Therefore, the addition of Co compounds during the molten salt process has no negative impact on the subsequent steps.

These processes using oxygen and molten Na_2CO_3 or Na_2SO_4 are expected to be developed in the future, because they can significantly reduce the cost of chemicals compared to the process using $NaNO_3$, and the reaction can be easily controlled.

New Recycling Processes Using Molten Sodium Hydroxides

The aforementioned molten salt processes use chemical reactions to oxidize W or WC. Although these processes are simple and cost effective, the reaction rate is difficult to control, the process using molten Na_2NO_3 tends to proceed excessively fast, whereas the other processes experience difficulty in obtaining a sufficient reaction rate. Therefore, we proposed an electrochemical W-recycling process using molten NaOH from super-hard alloy scraps [22–24]. In this process, super-hard alloy scraps were used as the anode, and W was dissolved as tungstate ions in molten NaOH, as shown schematically in Fig. 3. Here, the anodic, cathodic, and total reactions are

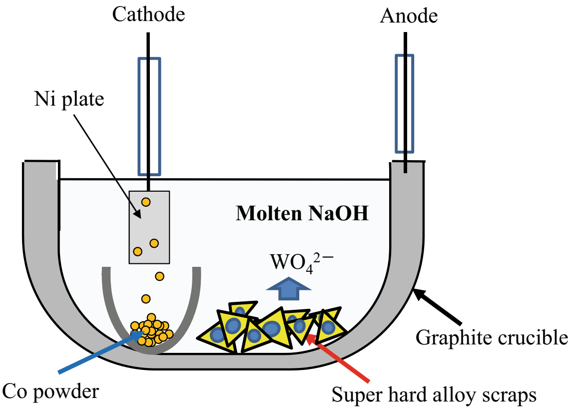

Fig. 3 Schematic drawing of anodic dissolution process of super hard alloy scraps in molten NaOH

described as follows:

$$WC + 7O^{2-} \rightarrow WO_4^{2-} + CO_3^{2-} + 10e^- \quad (3)$$

$$2OH^- + 2e^- \rightarrow H_2 + 2O^{2-} \quad (4)$$

$$WC + 10NaOH \rightarrow Na_2WO_4 + Na_2CO_3 + 5H_2 + 3Na_2O \quad (5)$$

Notably, the cathode reaction may result in Na precipitation, depending on the conditions. Cobalt, a major impurity, is also oxidized and dissolved, but most of the dissolved cobalt ions are reduced on the cathode and precipitated as Co powder. As reaction (5) proceeds, the tungsten content in the molten NaOH increases, and a Na_2WO_4 containing aqueous alkaline solution is obtained when the solidified NaOH melt is dissolved in water. Because this aqueous solution is essentially the same as that obtained using the conventional indirect method, W can be recovered by the usual process, as shown in Fig. 2b. Although this process has the disadvantage of consuming electric power, we believe it is advantageous for small-scale operations because the reaction is easy to control, and no harmful gas is generated. It has already been demonstrated that the oxidative dissolution of WC proceeds with a current efficiency of over 90% [22]. It was also confirmed that this process is greatly affected by the water content in the molten NaOH. For instance, when the water content is sufficiently low, the cathode reaction switches to Na electrodeposition. In addition, the solubility of Na_2WO_4 in molten NaOH significantly increases with water content [23]. We are currently investigating the precipitation of Na_2WO_4 powder from a W-enriched molten NaOH by controlling the water content in the melt, which enables the cyclic use of molten NaOH, as shown in Fig. 4 [24].

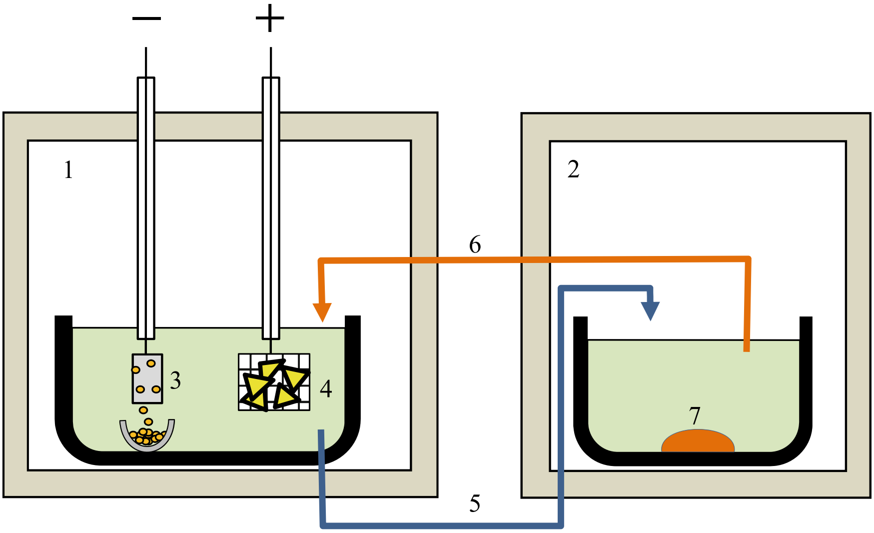

Fig. 4 Conceptual drawing of the new tungsten recycling process. 1. Anodic dissolution chamber kept at high partial pressure of water vapor and/or high temperature. 2. Precipitation chamber kept at low partial pressure of water vapour and/or low temperature. 3. Cathode of inert metals like Ni, on which H2 gas evolution and electrodeposition of powdery Co proceed. 4. Anode basket containing super hard alloy scraps, on which anodic dissolution of WC and binder metal of Co proceeds. 5. Flow path for tungstate ion-rich NaOH melt. 6. Flow path for tungstate ion-poor NaOH melt. 7. Precipitated Na2WO4

Conclusions

The molten salt process for tungsten recycling was reviewed. The molten salt process has been investigated as an alternative to the roasting and alkaline leaching process of super-hard alloy scrap in the conventional indirect method in which tungsten carbide is converted to water-soluble tungsten species. $NaNO_3$ is the most common oxidizing agent in this field, although the reaction is difficult to control. As a result of intensive investigation, one or more molten salt processes using $NaNO_3$ have been commercialized. The use of molten sulfates and carbonates is currently disadvantageous to the reaction rate, but this may be a candidate for a more economical and energy-saving process.

We proposed another molten salt process using molten hydroxide. In this process, the dissolution rate of super-hard alloy scrap was easily controllable, and Na_2WO_4 containing an aqueous solution was safely obtained. Further investigation is ongoing to simplify and reduce the cost of the process.

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