Original Article

Recovery of tungsten from WC–Co hard metal scraps using molten salts electrolysis

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\textbf{A B S T R A C T}

The recycling of WC–Co hard metal scraps has been taken into consideration in the literature, due to the release of toxic substances and long recovery process. In this study, the recovery of tungsten process, based on the molten salt electrolysis treatment of WC–Co hard metal scraps, was developed. The anode polarization curves were applied to investigate the dissolution of the WC–Co hard metal scrap. Then, the electrochemical behavior of tungsten and cobalt ions dissolved from WC–Co scrap anode, was studied by cyclic voltammetry (CV) and square wave voltammetry (SWV). The results demonstrated that the reduction of tungsten and cobalt ions occurred through a one-step process involving the transfer of two electrons. This process was achieved by the diffusion of tungsten and cobalt ions in the melts. Finally, the parameters, such as the electrolysis current, the electrolysis duration and temperatures, were applied to analyze the effect of different electrolysis conditions on the composition of recycled products. The results demonstrated that the electrolysis current and the electrolysis temperature, compared to electrolysis duration, have significant effects on the selectivity of tungsten recycling. Furthermore, the analysis of cathode products demonstrated that a tungsten powder of approximately 500 nm could be selectively recovered from WC–Co hard metal scrap with the electrolysis condition of 60 mA for 4 h at 1073 K in NaF-KF molten salt.

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1. Introduction

The tungsten carbide–cobalt (WC–Co) hard metal or cemented carbide, referred to as a composite material, is usually composed of WC particles embedded within a Co binder. The WC–Co hard metal is commonly utilized in the machining tools manufacturing, due to the corresponding excellent wear resistance, mechanical strength and toughness [1]. As the global population increases, the need for manufactured goods will also increase, and the consumption of tungsten carbide will grow [2]. However, both W and Co, which are rare metals, have significantly limited deposits globally and the majority of deposits are distributed in certain countries.
Therefore, the supply instability of W and Co to tool manufacturing industries is expected in the near future due to the corresponding rareness and localized deposits [3]. Especially regarding tungsten, the tungsten (W) is known as a strategic metal, which is widely utilized in the production of specialized tools, turbine-blade super alloys, penetrators, ammunitions, wear-resistant mechanical parts, catalysts, electrical and electronic components, incandescent lamp filaments and other high-tech products [4]. Therefore, the demand for tungsten is steadily increasing lately. Meanwhile, due to the severe form of tungsten ore resources exploitation and the serious decline in tungsten ore deposits around the world, effective recycling is the only solution to the problem of tungsten depletion [5]. In addition to natural resource protection, recycling also has other benefits, such as the reduction in the use of energy and chemicals in extracting tungsten and manufacturing of tungsten carbide, as well as reduction of waste [6]. Indeed, it is envisaged that recycling of tungsten carbide will considerably grow in the future because of the reasons mentioned above [2,6].

To recover the metallic values from WC–Co hard metals scraps, various processes, such as the zinc melt, the cold stream, the melt bath process, the soda roasting, the oxidation followed by reduction, and the oxidation followed by electrochemical and hydrometallurgical processes, have been developed [7–11]. In the widely used zinc melt process, the binder cobalt of the hard metal is alloyed by an attack of molten zinc [12]. The Zinc is then subsequently removed via through evaporation, leaving the WC as a solid sponge to be recovered as a powder by grinding. Moreover, the purity of the powder is not suitable for the particular application, due to contamination by undesirable elements [13]. Also, this process is required to be classified according to the composition of the cemented carbide. In hydrometallurgical processes, the binder cobalt is a dissolved as producing cobalt ions by different acidic solutions, leaving tungsten carbide in the residue [14–16]. In contrast, the rest of the tungsten carbide is not directly used for production of hard metals and requires further treatment to recover the tungsten value. Also, the incomplete leaching of cobalt and the presence of other metallic constituents, such as Ti, Ta, Nb, and Fe, etc., further complicate the composition of the leaching residue and make constitutive the recovery process complex. The aqua regia as a leaching agent dissolves the cobalt and simultaneously oxidizes the tungsten to tungstic acid, which precipitates as a residue. Furthermore, the use of hazardous hydrochloric acid and nitric acid causes environmental pollution and requires proper equipment for processing [17].

The molten salt electrolysis technology has been considered as an effective method for the preparation and recovery of high-melting point metals and corresponding alloys. Compared to other conventional approaches, the molten salt electrolysis has several advantages over the entire recovery of the WC–Co hard metal scrap:

- Direct separation and value metal powders acquisition, which promotes the recycling of metals.
- Molten salt medium can be recycled.

In this study, the WC–Co hard metals scrap was utilized as a consumable anode to selectively recover tungsten in the NaF–KF molten salt at 1073 K. Several electrochemical techniques, such as the anode polarization curves, cyclic voltammetry and the square wave voltammetry, were applied to investigate the electrochemical dissolution of WC–Co hard metal scrap and electrochemical behavior of the metal ion dissolved from the WC–Co hard metal scrap in the cathode. Consequently, in order to obtain the technology parameters of the selective tungsten recovery from the WC–Co hard metal scrap, the galvanostatic electrolysis was conducted with various electrolysis currents, various electrolysis durations and various temperatures in the NaF–KF melts.

2. Experimental

2.1. Materials

The WC–Co hard metal scrap utilized in this study was obtained from the Zigong Cemented Carbides Co. Ltd. The samples were cut into pieces (4 mm × 4 mm × 18 mm) prior to the experiment. The valuable metal contents were observed by the X-ray fluorescence (XRF) and the energy dispersive spectroscopy (EDS). Prior to the analysis, the WC–Co scrap was thoroughly polished with diamond papers and subsequently cleaned with ethanol in an ultrasonic bath.

Storage of all chemicals and sample preparations were handled in a glove box in purified Ar atmosphere where the oxygen content and moisture levels were maintained below 0.1 ppm. The electrolytic bath consisted in a mixture of NaF:KF (Aladdin 98% and 99.5%, respectively) with the eutectic composition (NaF:KF = 39.7%:60.3%), which was introduced into a graphite crucible. The crucible was loaded into a furnace, where the salts were treated as follows: after the furnace sealing, the temperature was heated to 473 K for 2 h under the condition of vacuum. The furnace temperature was subsequently retained at 473 K under vacuum for a period longer than 24 h for the trace moisture dehydration. Following, the mixture was heated to be melt at 1073 K, whereas high purity argon gas (99.9%pct) was injected into the vessel for an inert atmosphere to be retained.

2.2. Experimental equipment

The experimental device is presented in Fig. 1. The cell consisted of a high pure graphite crucible (99.9 wt.%), placed in the furnace, and closed by a stainless steel lid cooled by water circulation. The experiments were performed under an inert argon (below 0.1 ppm O₂) atmosphere with the flow rate of 50 ml/min. The cell was heated by a programmable furnace and the temperature measurement was executed by a Pt-Rh thermocouple with an accuracy of ±2 K.
2.3. Analytical method

The utilized analytic electrochemical techniques (cyclic voltammetry and square-wave voltammetry) required a three-electrode set-up. A platinum wire (Φ0.5 mm) and the WC–Co scrap were utilized as the working electrodes for the electrochemical behavior investigation during the entire electrolysis process. Also, a platinum wire was selected as a quasi-reference electrode Pt/PtO_x/O^2−, due to the corresponding inertness with respect to the metal ions in the molten salts [18]. The active surface of the platinum electrode was determined subsequently to each experiment by the immersion depth measurement in the bath. The auxiliary electrode was a graphite rod of 3 mm in diameter.

All electrochemical studies and electrolysis experiments were performed with the PARSTAT 4000 electrochemical workstation, along with the Versa Studio software package (Advanced Measurement Technology, Inc., USA). The anode polarization curves (scan rate: 100 mV/s) were initially applied to investigate the dissolution of the WC–Co scrap hard metal. Subsequently, the cyclic voltammetry and the square wave voltammetry were selected for the cathodic process of tungsten and cobalt ions in the NaF–KF molten salt.

The tungsten powder selective recovery experiment was executed in the NaF–KF salt at 1073 K. The WC–Co scrap and a nickel plate (8 × 30 × 0.1 mm) were utilized as the anode and the cathode, respectively. Following constant-current electrolysis, the product on the cathode was washed in an ultrasonic tank containing a solution of water and ethanol for the salt dissolution. Finally, the cathode products were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM, Quanta FEG 650), energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM).

3. Results and discussion

3.1. WC–Co hard metal scrap characterization

As presented in Fig. 2, the WC–Co hard metal scrap was characterized by SEM (BSE mode) and EDS, to evaluate the corresponding micro-morphology, the type and content of the metal elements. As demonstrated in Fig. 2a, the WC–Co hard metal scrap anode displayed a uniform morphology, where the gray white substances were WC particles and the black substances were Co phases. From the element mapping of the anode in Fig. 2b–d, it could be observed that the anode surface mainly contained a high amount of W, C and a low amount of Co, without other addition element. According to the EDS spectrum analysis (Fig. 2e) and XRF analysis (Table 1) results on the WC–Co scrap anode surface, it was demonstrated that the W retained a high proportion compared to the C and Co, indicating that the selective recovery of tungsten from the WC–Co hard metal scraps was considerably necessary.

3.2. The anode polarization of WC–Co scrap hard metal anode

The anode polarization curves of WC–Co scrap with a scan rate of 100 mV/s in Fig. 3 was determined whether the WC–Co scrap hard metal anode can be dissolved electrochemically in the NaF–KF melt at 1073 K. In comparison with Pt wire and W rod, it can be clearly seen that the current rapidly increases with the increase in potential from −0.1 V (vs. Pt), which was attributed to a electrochemical dissolution of WC–Co scrap anode in the melts [19].
3.3. Cyclic voltammetry of tungsten and cobalt ions from WC-Co scrap

To investigate the electrochemical behavior of cobalt and tungsten ions, the galvanostatic electrolysis at 60 mA for 4 h was subsequently performed to produce tungsten and cobalt ions in the molten salts (Fig. 4). The cyclic voltammogram in the blank NaF–KF eutectic melt prior to and following the WC–Co electrolysis at 60 mA for 4 h is presented at 1073 K in Fig. 4a. A potential scan was performed in the purified NaF–KF melt by a Pt wire electrode and the potential window was subsequently recorded. It was clear that no peaks existed on the voltammogram, during the negative potential scan. Subsequently to electrolysis, two sharp cathodic peaks with cathodic return peaks were observed at $-0.47$ V and $-0.57$ V vs. Pt, $-0.06$ V and $-0.29$ V vs. Pt, respectively. These redox waves corresponded to the reduction of tungsten and cobalt ions and the dissolution of the deposited metallic tungsten and cobalt. The electroreduction of the tungsten and cobalt ions proceeded with the one-step electrolysis process.

In order to determine the reduction peaks of tungsten and cobalt ions, the pure tungsten rod and cobalt scrap were utilized as sacrificial anodes, to produce tungsten and cobalt ions and to investigate the corresponding electrochemical behavior. Under the same electrolysis condition, the tungsten rod
and the cobalt scrap were separately electrochemically dissolved as tungsten and cobalt ions in the NaF–KF molten salts at 1073 K. The cyclic voltammogram was applied to distinguish the reduction potential of tungsten and cobalt ions. From Fig. 4b, it could be observed that the reduction potential of the metal ions in the melts were $-0.29$ V vs. Pt and $-0.57$ V vs. Pt. Fig. 4c and d displays that the reduction potentials of tungsten and cobalt ions were $-0.23$ V vs. Pt and $-0.56$ V vs. Pt following the electrochemical dissolution of the pure tungsten rod and pure cobalt scrap at the electrolysis current of 60 mA for 4 h. The dissolution had similar results of the cyclic voltammetry consequence of the WC–Co scrap anode electrochemical dissolution. Therefore, it could be concluded that the R2 reduction peak was the cobalt ion reduction peak and the R1 reduction peak was the tungsten ion reduction peak.

Cyclic voltammogram measurements with a wide scan rate range were executed to further study the redox reaction reversibility. Fig. 5a presents the cyclic voltammograms at various scan rates following the WC–Co scrap anode electrolys. As the cathodic potential was independent of the sweep rate, it could be concluded that the reduction process of tungsten and cobalt ions was reversible.

The relationship between the cathodic peak current and the square root of the scan rate is depicted in Fig. 5b and c. On the Pt electrode at 1073 K, the plots were linearly passing through the zero point, indicating that the reduction of tungsten and cobalt ions was controlled by ion diffusion in the molten salts. Fig. 5b and c displays that the cathodic peak potential of R1 and R2 remained nearly constant regardless of scan rates, confirming the reversibility of the reduction process of the tungsten and cobalt ions.

### 3.4. Square wave voltammetry of tungsten and cobalt ions from WC–Co scrap

Regarding the square wave voltammetry for the ideal situation of a reversible system, described in details by Osteryoung...
et al. [20,21], the potential-current curve had a Gaussian shape with a peak at a potential, close to the half-wave potential for the ionized species. The mathematical expression had the following characteristics:

1. The width of the peak \(W_{1/2}\) at half the corresponding height depends on the number of electrons \(n\) exchanged at the operating temperature.

\[
W_{1/2} = \frac{3.52RT}{nf}
\]  

(1)

where \(R\) is the ideal gas constant; \(T\) is the absolute temperature and \(F\) is the Faraday constant; 3.52 is dimensionless.

2. The peak current \(i_p\) varied linearly with the concentration of the electroactive species and with the square root of the frequency \(f\), according to equation:

\[
i_p = nFA\frac{1 - \Gamma}{1 + \Gamma}\sqrt{\frac{Df}{\pi}} = \exp\left(\frac{nF\Delta E}{2RT}\right)\frac{nFA}{1 + \Gamma}\sqrt{\frac{Df}{\pi}}
\]  

(2)

where \(\Delta E\) is the amplitude of the square wave potential; \(A\) is the surface area of the electrode; \(D\) is the diffusion coefficient and \(C_0\) is the bulk concentration of the electroactive species.

The square wave voltammetry was applied to investigate the transfer electrons number of cobalt and tungsten ions from the WC–Co scrap anode in the NaF–KF melts, following the completion of galvanostatic electrolysis at 60 mA for 4 h. Fig. 6a presents the obtained typical square wave voltammograms. In the negative potential scan, two cathodic peaks appeared at \(-0.28\) V (vs.) and \(-0.57\) V (vs.), respectively, which were consistent with the cyclic voltammograms results. The two cathodic waves in Fig. 6a were bell-shaped and symmetrical approximately as the half-wave potential, whereas two peaks could be utilized for the quantitative analysis. Once again, this demonstrated the significant advantage of square wave voltammetry against cyclic voltammetry and the corresponding ability to accurate quantify an electrochemical process. By the width measurement at the mid-height of each peak at various frequencies (Tables 2 and 3), it was possible, through Eq. (1), to determine the average electron number that must have been exchanged \(n\):

Peak (R1): \(n = 2\)
Peak (R2): \(n = 2\)

It could therefore be concluded that the electro-reduction of tungsten and cobalt ions from the WC–Co scrap anode in the
NaF–KF molten salts, proceeded through the following one-step process:

\[
\begin{align*}
W^{2+} + 2e^- &= W \quad (3) \\
Co^{2+} + 2e^- &= Co \quad (4)
\end{align*}
\]

Based on Eq. (2), the peak height and the frequency square root were indicated by the relationship, as presented in Fig. 6b and c. The reversibility could be checked by the maximum current peak plot of the current peak vs. the square root of frequency of the square wave signal. The obtained straight lines confirmed that the reduction of W(II)/W(0) and Co(II)/Co(0) was a diffusion-controlled process. Also, since the anodic peaks R1 and R2 remained constant over a specific frequency range, it was demonstrated that the reduction of tungsten and cobalt ions was a reversible process. This was consistent with the cyclic voltammetry results.

### 3.5 Recovery of tungsten from WC–Co hard metal scrap

#### 3.5.1 Effect of electrolysis current on product composition

The galvanostatic electrolysis was executed for the selective recovery of tungsten from the WC–Co hard metal scrap. Different electrolysis currents were applied on the system at 1073 K for 4 h. The cell voltage–time curves with various currents are presented in Fig. 7a. The cell voltage increased as the current increased. During the electrolysis, the cell voltage remained steady first and then decreased gradually, indicating that anodic dissolution was not a stable process. The photographs of the anode before and after electrolysis with 60 mA for 4 h are also shown in Fig. 7a, indicating obviously visible change in the shape can be observed. The SEM micrograph of anode after electrolysis shows that the residual structure on the surface has a “sponge-like” shape. These results indicate that the WC–Co hard metal scrap was electrolyzed in NaF–KF melts at 1073 K. Fig. 7b presents the product that was obtained at the cathode subsequently to the galvanostatic electrolysis currents. The product treated at the 20 mA current displayed peaks that corresponded to the metallic Co and metallic W. As the current increased, the peaks of W$_2$C and W were observed at the currents of 40, 60, 80 and 100 mA, respectively. In contrast, the peak of Co disappeared. Two kinds of explanations illustrated this phenomenon. The first explanation was that only tungsten dissolved from the WC–Co scrap. The second explanation was that cobalt ion concentration was significantly low to precipitate at the cathode. In order to confirm the reason for the disappearance of cobalt, the ICPAES was applied to investigate the concentration of metal ions in the molten molten salts. According to the results, the concentrations of tungsten ion and cobalt ions are 4.53 $\times$ 10$^{-6}$ mol/cm$^3$ and 2.75 $\times$ 10$^{-7}$ mol/cm$^3$ under the condition of electrolysis current 60 mA. Based on these results, the reason for disappearance of the cobalt was that the significantly low cobalt ion concentration is difficult to precipitate at the cathode. Moreover, according to Nakajima [22], potassium fluoride was favorable for tungsten ion deposition in the cathode. Also, the occurrence of W$_2$C on the cathode occurred due to the reaction between W and C drifted from anode, which occurred again [23].

The X-ray photoelectron spectroscopy (XPS) was performed and identified the electrodeposited product as the metallic

<p>| Table 2 – The date of square wave voltammetry for R1. |</p>
<table>
<thead>
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<th>Frequency (Hz)</th>
<th>Half width (V)</th>
<th>Transferred electrons</th>
</tr>
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<td>5</td>
<td>0.187</td>
<td>1.74</td>
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<tr>
<td>10</td>
<td>0.192</td>
<td>1.69</td>
</tr>
<tr>
<td>15</td>
<td>0.203</td>
<td>1.60</td>
</tr>
<tr>
<td>20</td>
<td>0.199</td>
<td>1.63</td>
</tr>
<tr>
<td>25</td>
<td>0.198</td>
<td>1.64</td>
</tr>
</tbody>
</table>

<p>| Table 3 – The date of square wave voltammetry for R2. |</p>
<table>
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<th>Frequency (Hz)</th>
<th>Half width (V)</th>
<th>Transferred electrons</th>
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<td>20</td>
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<td>2.04</td>
</tr>
<tr>
<td>25</td>
<td>0.155</td>
<td>2.09</td>
</tr>
</tbody>
</table>

Fig. 7 – (a) Potential-time curves at various electrolysis currents with the area 1.12 cm$^2$ of WC–Co scrap anode (1073 K) (insert: the photographs and SEM micropicture of WC–Co scrap before electrolysis and after electrolysis with 60 mA for 4 h). (b) XRD patterns of cathode product obtained at various electrolysis currents.
tungsten. The XPS spectra of the electrodeposited product formed at 60 mA is presented in Fig. 8a. In this figure, the peaks of 4f 7/2 and 4f 5/2 at 31.32 eV and 33.40 eV corresponded to the peak of tungsten [24]. The SEM image of the cathode products with 60 mA for 4 h and EDS analysis are presented in Fig. 8b and c. The particle size of the tungsten powders was observed to be lower than 1 um at 60 mA, whereas the crystallized particles were presented as individual and continuous. The EDS results demonstrated that the electrolyzed sample was essentially composed of tungsten metals. These results confirmed that the tungsten was selectively separated from the WC–Co and obtained on the cathode. Fig. 8d presents the TEM photographs of the tungsten powder. Apparently, the tungsten powder diameter was approximately 500 nm. The selected area electron diffraction (SAED) pattern obtained by the electric beam focus on a single rod is displayed in Fig. 8e, which displayed diffused rings, indicating that the tungsten powders were composed of polycrystalline tungsten nanoparticles. Fig. 8g presents a typical HRTEM image, where the lattice structure of the tungsten nanoparticles could be clearly observed. The lattice fringe was 0.22 nm, which was similar to the (110) crystal lattice of the tungsten orthorhombic structure. From the HRTEM results, it was further confirmed that the tungsten microspheres were orthorhombic phases, as indexed by XRD.

3.5.2. Effect of electrolysis duration on product composition

Based on the aforementioned experimental results, the electrolysis duration effects on the composition of the product were studied with 40 mA at 1073 K. The WC–Co scrap anode dissolved as cobalt ions and tungsten ions during the electrolysis. Subsequently, the ions discharged and the cobalt and tungsten were possibly deposited on the cathode. Moreover, due to the cobalt ion lower concentration in the molten salts, the cobalt is difficult to precipitate at the cathode. The XRD patterns of the cathode products for various electrolysis durations with 40 mA at 1073 K are presented in Fig. 9. It could be observed that the tungsten was obtained at the cathode, which indicated that the increase of electrolysis duration has no apparent effect on the cathodic product compositions. Fig. 10
The electrolysis temperature increased, the peaks of cobalt disappeared and the tungsten became the major phase. The SEM images of the resulting products at the cathode were polarized at 40 mA for 4 h under various electrolysis temperatures in the range of 1048–1123 K (Fig. 12). As the electrolysis temperature increased, the tungsten particle size of the products became higher.

### 4. Conclusions

A new process without negative impact on the environment was investigated, to recover the valuable metal tungsten from the WC-Co hard metals scrap. The WC-Co scrap and NaF–KF molten salts were utilized as the consumed anode and the electrolyte, respectively. The anodic polarization curves were used to validate the feasibility of electrochemical dissolution of the WC-Co hard metal scrap. Furthermore, the electrochemical behavior of the tungsten and cobalt ions, dissolved from WC-Co scrap anode, was studied in the eutectic NaF–KF mixture at the Pt electrode. The cyclic voltammetry and square-wave voltammetry demonstrated that the tungsten and cobalt ions reduction occurred through a one-step process, involving the transfer of two electrons. This process was controlled by the tungsten and cobalt ions diffusion in the melts. The galvanostatic electrolysis was executed for the recovery of tungsten from the WC-Co hard metal scraps and the results indicated that the electrolysis current and electrolysis temperature compared to the electrolysis duration, had significant effect on the tungsten recycling under the same electrolysis condition. Subsequently to the galvanostatic electrolysis with 60 mA for 4 h at 1073 K, the tungsten powder of...
Fig. 12 – SEM images of the products obtained at cathode after galvanostatic electrolysis at different electrolysis temperature with 40 mA: (a) 1048 K, (b) 1073 K, (c) 1098 K and (d) 1123 K.

approximately 500 nm was selectively obtained on the cathode.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

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