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Title: Separation of tungsten and cobalt from WC-Co hard metal wastes using ion-exchange and solvent extraction with ionic liquid

Article Type: Research Paper

Keywords: Ion exchange; Ionic liquid; Solvent extraction; Tungsten; WC-Co hard metal

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Abstract: Recently, the development of a process to separate W and Co from tungsten carbide-cobalt (WC-Co) hard metal wastes has become important. In this study, we proposed a novel hydrometallurgical process involving the following steps: pretreatment, leaching, ion exchange, and two-step solvent extraction (I) and (II) using ionic liquids (ILs). First, an AlCrN film coating was completely removed from a WC-Co hard metal sample by leaching in a H₂SO₄-H₃PO₄ mixed acid medium at 423 K for 120 h. Then, the sample was oxidized at 1173 K for 10 h and XRD analysis showed that WO₃ and CoWO₄ were generated during this oxidization. After the oxidization, the leaching reaction $WO_3 + 2LiOH \rightarrow WO_4^{2-} + 2Li^+ + H_2O$ smoothly proceeded in leaching solution of 0.1 mol/L LiOH at 343 K for 19 h and the stoichiometry of WO₃:LiOH was 1:2, which was consistent with that of the leaching reaction. Further, after the leaching step was completed, it was beneficial to exchange H⁺ and Li⁺ in the leaching solution using a cation exchange resin. Solvent extraction was performed using triethyl-n-pentyl phosphonium bis(trifluoromethylsulfonyl)amide as the IL, and tri-n-octylamine was employed as the extractant for the selective separation of W(VI) for solvent extraction (I). The extraction percentages (E) of W(VI) and Co(II) were >95% and <2.5% at pH = 1.0, respectively, and the selective extraction of W(VI) was confirmed in this study. The extraction mechanism of W(VI) was based on the ion association reaction $n[R_3N]_{org} + [HxWyOzn]_{aq} + n[H^+]_{aq} \rightleftharpoons [(R_3NH)_nHxWyOz]_{org}$. In solvent extraction (II), a PC-88A/[P2225][NTf₂] system was used for the effective extraction of Co(II) at pH > 4.3. The slope analysis results showed that the extraction mechanism was governed by the cation exchange reaction $[Co^{2+}]_{aq} + 2[(HL)_2]_{org} \rightleftharpoons [CoL_2 \cdot 2HL]_{org} + 2[H^+]_{aq}$. A series of novel hydrometallurgical process using IL enabled us to demonstrate that W(VI) and Co(II) were efficiently recovered from WC-Co hard metal wastes.

1 Dear Prof. B. A. Wills

2 Editor of Minerals Engineering

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5 Thank you for sending e-mail and many valuable reviewer comments.

6 The comments for each reviewer about the revised manuscript were written as follows.

7
8 We hope that the revised manuscript will be suitable for the publication.

9 Sincerely yours.

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14 Dr. Masahiko Matsumiya

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For Reviewer 1

Thank you for sending many useful comments.

According to your comments, the revised manuscript was corrected as follows.

Reviewer #1: This article is about the separation of tungsten and cobalt from WC-Co hard metal wastes using ion-exchange and solvent extraction with ionic liquid. This research presents interesting results. It merits to be published in Minerals Engineering if the authors clarify the following points.

1. The structure figure and preparation of IL should be given.

According to your suggestion, the structure figure of IL was added in new Fig. 2 in the revised manuscript.

The preparation of IL was also added in the revised manuscript. (p.5L20-L25)

2. Error bars should be given in the figures

According to your suggestion, the error bar was added in new Fig. 7 in the revised manuscript.

3. IR spectra may be used to study the extraction mechanism

Based your suggestion, we tried to measure IR spectrum for aqueous and organic phases to study the extraction mechanism. However, we did not obtain the effective results from IR spectrum. Therefore, we tried to measure UV-Vis spectrum for aqueous and organic phases. As a result, we found that it was better to confirm the W(VI) complex state of aqueous and organic phases from UV-Vis analysis. The UV-Vis result was added in new Fig.9. The experimental condition and the related comments were also added in the revised manuscript. (p.6L3-L6, p.9L22-L27)

4. The unit of M should be revised to be mol/l

According to your suggestion, the unit of M was modified to be mol/L in the revised manuscript.

5. Why equation 10 is called as an anion exchange process? It is an ion association extraction mechanism.

According to your suggestion, the name of the exchange process was modified in the revised manuscript. (p.2L17, p.9L12, p.11L18)

6. The stripping and recycling of IL-based extraction system should be investigated.

Based on your suggestion, we additionally investigated the stripping and recycling of IL-based extraction system at fifth cycles. The stripping and recycling results were added in new Table 4 in the revised manuscript. The experimental condition and the related comments were also added in the revised manuscript. (p.3L25-L26, p.6L23-p.7L26, p.10L20-p.11L3)

The other revised sentences were marked with red letter in the revised manuscript.

We hope that the revised manuscript will be suitable for the publication.

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Highlights

- A novel hydrometallurgical process was consisted of two step solvent extraction using ionic liquid.
- W(VI) was selectively extracted from WC-Co hard metal by $[R_3N]/[P_{2225}][NTf_2]$, $R=(CH_2)_7CH_3$.
- The extraction mechanism of W(VI) was based on the ion association reaction.
- Co(II) was effectively extracted by PC-88A/ $[P_{2225}][NTf_2]$ at $pH>4.3$ after removal of W(VI).
- $[R_3N]/[P_{2225}][NTf_2]$ solvent was repeatedly applied on extraction-stripping process at 5th cycles.

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13 Separation of tungsten and cobalt from WC-Co hard metal wastes
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15 using ion-exchange and solvent extraction with ionic liquid
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ABSTRACT

Recently, the development of a process to separate W and Co from tungsten carbide-cobalt (WC-Co) hard metal wastes has become important. In this study, we proposed a novel hydrometallurgical process involving the following steps: pretreatment, leaching, ion exchange, and two-step solvent extraction (I) and (II) using ionic liquids (ILs). First, an AlCrN film coating was completely removed from a WC-Co hard metal sample by leaching in a H₂SO₄-H₃PO₄ mixed acid medium at 423 K for 120 h. Then, the sample was oxidized at 1173 K for 10 h and XRD analysis showed that WO₃ and CoWO₄ were generated during this oxidization. After the oxidization, the leaching reaction $\text{WO}_3 + 2\text{LiOH} \rightarrow \text{WO}_4^{2-} + 2\text{Li}^+ + \text{H}_2\text{O}$ smoothly proceeded in leaching solution of 0.1 mol/L LiOH at 343 K for 19 h and the stoichiometry of WO₃:LiOH was 1:2, which was consistent with that of the leaching reaction. Further, after the leaching step was completed, it was beneficial to exchange H⁺ and Li⁺ in the leaching solution using a cation exchange resin.

Solvent extraction was performed using triethyl-*n*-pentyl phosphonium bis(trifluoromethylsulfonyl)amide as the IL, and tri-*n*-octylamine was employed as the extractant for the selective separation of W(VI) for solvent extraction (I). The extraction percentages (*E*) of W(VI) and Co(II) were >95% and <2.5% at pH = 1.0, respectively, and the selective extraction of W(VI) was confirmed in this study. The extraction mechanism of W(VI) was based on the ion association reaction $n[\text{R}_3\text{N}]_{\text{org}} + [\text{H}_x\text{W}_y\text{O}_z^{n-}]_{\text{aq}} + n[\text{H}^+]_{\text{aq}} \Leftrightarrow [(\text{R}_3\text{NH})_n\text{H}_x\text{W}_y\text{O}_z]_{\text{org}}$. In solvent extraction (II), a PC-88A/[P₂₂₂₅][NTf₂] system was used for the effective extraction of Co(II) at pH > 4.3. The slope analysis results showed that the extraction mechanism was governed by the cation exchange reaction $[\text{Co}^{2+}]_{\text{aq}} + 2[(\text{HL})_2]_{\text{org}} \Leftrightarrow [\text{CoL}_2 \cdot 2\text{HL}]_{\text{org}} + 2[\text{H}^+]_{\text{aq}}$. A series of novel hydrometallurgical process using IL enabled us to demonstrate that W(VI) and Co(II) were efficiently recovered from WC-Co hard metal wastes.

Key words: Ion exchange; Ionic liquid; Solvent extraction; Tungsten; WC-Co hard metal

1. Introduction

Tungsten carbide-cobalt (WC-Co) hard metal or cemented carbide is a composite material usually comprising WC particles embedded within a Co binder. This hard metal is commonly used for manufacturing tools because of its good mechanical strength and wear resistance (Brookes, 1996). The Co content in WC-Co hard metal machining tools is usually between 4 and 12 wt%. Because of the harmful environmental effects, each component of the hard metal must be separated. Some hydrometallurgical methods to selectively recover W or Co from WC-Co scraps and to process WC-Co scraps to obtain W metal or ammonium paratungstate have been proposed (Gaur, 2009).

Solvent extraction is a very useful technique to recover tungsten from its leachates (Lassner, 1995, Pandey et. al., 2001). Aliphatic amines have been widely employed as extractants (Carvalho et. al., 1991, Coca et. al., 1990, Palant et. al., 1998, Sato et. al., 1995), and tertiary amines (Gerhardt et. al., 2001) have been most frequently reported in literature. The concentration of the extractant must be low (<10 vol.%) to avoid emulsification (Zhang et. al., 1996). Kerosene is widely employed as a diluent; however, the presence of phase modifiers is usually necessary because amino tungstate complexes are not very soluble in the organic phase. Recently, numerous studies aimed at the development of a solvent-based separation process have been conducted. In the present study, in a departure from the conventional solvent extraction approach, we investigated the feasibility of using a phosphonium ionic liquid (IL) as the medium for the separation of W from the leaching solution. A well-known amine with the molecular formula (R_3N , $R=(CH_2)_7CH_3$), tri-*n*-octylamine (TOA), was chosen as the preferred extractant because it offers many advantages such as negligible solubility in the aqueous phase, high boiling point, low density, low cost, and easy availability (Lide, 1993).

The objective of this study is to develop a novel hydrometallurgical process to separate **W(VI)** and **Co(II)** from each other and from WC-Co hard metal, as shown in **Fig. 1**; this process involves the following steps: pretreatment, leaching, ion exchange, and two-step solvent extraction (I and II) using ILs. **Moreover, the reuse of $[R_3N]/IL$, $R=(CH_2)_7CH_3$ solvent was evaluated by solvent extraction and stripping process at 5th cycles.**

2. Experimental

2.1 Pretreatment

The rectangular WC-Co hard metal wastes (12mm×12mm×4.76mm) were used as a sample in this study. An AlCrN film was coated on the surface of a WC-Co sample, because its resistance to wear and oxidation during cutting extended the design life of cutting tools. This AlCrN film coating was undesirable for the complete oxidization of the WC-Co sample at high temperature, which generates WO₃ and CoWO₄, because it made the sample highly resistant to oxidation even at 1173 K (Chim et. al., 2009, Gu et. al., 2012). The WC-Co sample with AlCrN film coating was introduced in a Teflon beaker including a H₂SO₄-H₃PO₄ (H₂SO₄ : H₃PO₄=1 : 1) mixed acid solution. The leaching mixed acid solution was rotated at rates up to 300 rpm at 423 K for 120 h. After the removal of AlCrN film, the WC-Co sample was cleaned in a distilled water. The surface morphology and composition of the AlCrN film coating and WC-Co sample were analyzed by scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDX, JSM-6510LA, JEOL Ltd.). Then, the WC-Co fragments obtained after removal of the AlCrN film coating were heated to 1173 K at 5 K min⁻¹ in an oxygen atmosphere for 10 h. The oxygen flow rate was 150 mL s⁻¹. The oxidized WC-Co sample was then pulverized to particles with a diameter of approximately 3 μm using a planetary ball mill.

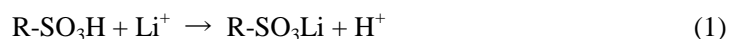
2.2 Leaching

The 0.1 mol/L LiOH solution was selected to dissolve W present in the oxidized WC-Co sample. The 10.0 g of the oxidized WC-Co powder was added to 500 mL of 0.1 mol/L LiOH solution. The leaching solution was then agitated at rates up to 500 rpm at 343 K for 19 h. After W dissolution, the solutions were passed through a 1-μm-pore membrane filter to screen the undissolved oxidized residue. The concentration of W(VI) in the leaching solution was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPE-9000, Shimadzu Co.). The changes in pH with elapsed leaching time was precisely measured by a high-precision digital pH

meter (MM-43X, DKK-TOA Corp.). The measured pH in the saturated leaching solution was 7.55.

2.3 Ion exchange

After leaching, exchange of H⁺ and Li⁺ in the leaching solution was performed, as the following solvent extraction was performed under acidic conditions to protonate the extractant. The ion exchange reaction of the cation exchange resin (IR120B, ORGANO Corp.) can be expressed as follows:



According to this reaction, the amount of ions exchanged was controlled by the time of ion exchange for the constant initial amount of the cation exchange resin. The decreasing amount of Li⁺ in the leaching solution was confirmed from the changes in pH. Several sample solutions pH values of 7.55–1.0 were prepared by the ion exchange reaction.

2.4 Solvent extraction

In this study, the solvent extraction process consisted of two steps to effectively separate **W(VI)** and **Co(II)** from the leaching solution. For the solvent extraction processes (I) and (II), TOA (Wako Pure Chemical Industries, Ltd., >98.0%) and PC-88A (DAIHACHI Chemical Industry Co. Ltd.) were selected as the extractants, respectively. The IL triethyl-*n*-pentyl phosphonium bis(trifluoromethyl-sulfonyl)amide ([P₂₂₂₅][NTf₂]) as shown in **Fig. 2** was synthesized from the metathesis reaction of [P₂₂₂₅]**Br** (Nippon Chemical Industrial Co., Ltd., >99.5%) with Li[NTf₂] (Kanto Chemical Co., Inc., 99.7%) in distilled water at 343 K (Tsunashima et. al., 2007, Tsunashima et. al., 2011). The synthesized [P₂₂₂₅][NTf₂] was purified by stirring with distilled water to remove lithium and bromide ions, followed by evaporation at 423 K for 24 h. The obtained [P₂₂₂₅][NTf₂] was then dried under high vacuum <-0.1 MPa at 393 K for 48 h. The [P₂₂₂₅][NTf₂] and kerosene were used as the diluent for both stages. For solvent extraction (I), the aqueous phase after the ion

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2 exchange reaction acted as the solution. The concentration of $[H_xW_yO_z^{n-}]$ and Co^{2+} in the 0.1
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4 mol/L LiOH solution was 4.7×10^{-2} mol/L and 8.5×10^{-3} mol/L, respectively. The TOA
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6 concentration in the organic phase was 1.0 mol/L. The pH of the aqueous solution was varied from
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8 1.0 to 6.8 to investigate the extraction behavior. In order to confirm the complex state of W(VI),
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10 the absorption spectrum of W(VI) in aqueous and organic phases was measured by UV-Vis
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12 spectrometer (Perkin Elmer, Lambda750). In this spectroscopic measurement, a quartz cell with
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14 1.0 cm optical path length was used in the wavelength region of 200-1000 nm.
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17 For solvent extraction (II), the solution after the removal of W(VI) complexes using TOA acted
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19 as the aqueous phase. The concentration of PC-88A was 0.1 mol/L in the PC-88A/[P₂₂₂₅][NTf₂]
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21 extraction system. For the stoichiometry-related slope analysis, the pH of the aqueous phase was
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23 varied from 2.0 to 4.4. All extraction processes were performed at 298 K with an aqueous to
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25 organic phase ratio of 1:1 by volume. The solutions were placed in a sampling tube and shaken for
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27 5 min using a direct mixer. The concentrations of the metal ions in the aqueous phase before and
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29 after the equilibration were measured by ICP-AES. The concentration of the metal ions in the
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31 organic phase after the equilibration was calculated using a mass balance equation. The
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33 distribution ratio (*D*) and extraction efficiency (*E*) were defined as follows:
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$$D = \frac{[M]_{aq,i} - [M]_{aq,f}}{[M]_{aq,f}} \quad (2)$$

$$E (\%) = \frac{[M]_{aq,i} - [M]_{aq,f}}{[M]_{aq,i}} \times 100 \quad (3)$$

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47 where $[M]_i$ and $[M]_f$ represent the initial and final concentrations of the metal ions in the aqueous
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49 phase, respectively, and the subscript aq denotes the aqueous phase.
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52 In order to evaluate the reuse of $[R_3N]/[P_{2225}][NTf_2]$, $R=(CH_2)_7CH_3$ solvent system, a recycling
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54 run consisting of solvent extraction and stripping for 5th cycles was performed. For solvent
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56 extraction, 1.0×10^3 mg L⁻¹ W(VI) was used as the aqueous phase. The volume ratio (A/O) of the
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58 aqueous and organic phase was maintained at A/O = 1.0. After solvent extraction, the stripping
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2 was performed for three kinds of media (HCl, NH₃ and NaOH aqueous solution) with different
3 concentrations (0.5, 1.0, 1.5 and 3.0 mol/L). After stripping, in the second solvent extraction, the
4 new aqueous phase containing 1.0×10³ mg L⁻¹ W(VI) was introduced into the organic phase with
5 A/O = 1.0. After the second solvent extraction, the second stripping was performed with the same
6 conditions. Thus, the procedure for solvent extraction and stripping was repeatedly carried out for
7 5th cycles. After the fifth continuous extraction-stripping procedure, the metal concentration in the
8 organic phase for each cycle was determined by ICP-AES.
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10 11 12 13 14 15 16 17 18 19 **3. Results and discussions**

20 21 3.1 Pretreatment

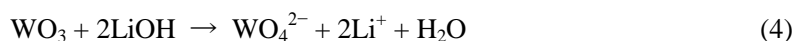
22
23 The AlCrN film coating on the WC-Co hard metal sample was gradually leached using the
24 H₂SO₄-H₃PO₄ mixed acid medium. The surface morphology of the AlCrN film coating and the
25 WC-Co sample after removal of the coating was analyzed by SEM, as shown in **Figs. 3(a)** and **(b)**,
26 respectively. The surface morphology before and after the removal treatment were completely
27 different. The composition result evaluated by EDX was tabulated in **Table 1** and we confirmed
28 the complete removal of the AlCrN film coating.
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31 After removal of the AlCrN film coating, the WC-Co sample was heated in an oxygen
32 atmosphere at 1173 K for 10 h. The XRD profiles of the WC-Co sample before and after
33 oxidization are shown in **Fig. 4**. For the former, a sharp WC peak (00-025-1047) was detected,
34 whereas for the latter, WO₃ (01-083-0950) and CoWO₄ (00-015-0867) peaks were clearly observed.
35 Thus, we confirmed that the WC-Co sample was completely oxidized to generate WO₃ and CoWO₄.
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37 38 39 40 41 42 43 44 45 46 47 48 49 3.2 Leaching

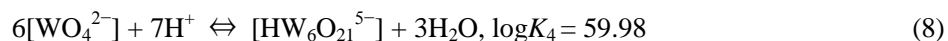
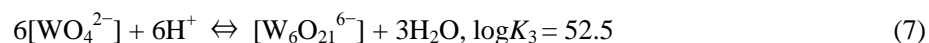
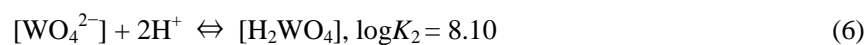
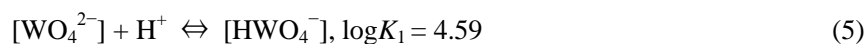
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51 The leaching behavior of W present in the oxidized WC-Co sample was investigated and the
52 amount of W leached by the 0.1 mol/L LiOH solution with respect to leaching time is shown in **Fig.**

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55 **5.** The leaching reaction can be expressed as follows:
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The amount of W leached in 500 mL 0.1 mol/L LiOH solution (LiOH: 5.0×10^{-2} mol) gradually increased with leaching time and reached saturation at 7 h. The pH value of the leaching solution gradually decreased with leaching time and reached a constant value at 7 h. Finally, the saturated amount of W was 4.284 g (W: 2.33×10^{-2} mol) and the final pH was 7.55. Also, the molar stoichiometric ratio of WO_3 :LiOH was 1:2.1, which was consistent with that suggested by equation (4).

Furthermore, it is important to understand the distribution of tungstate ions in a wide pH range as listed in **Table 2**. It is known that $[\text{WO}_4^{2-}]$ is stable in alkaline solutions and reacts in acidic media based on the following equilibria:



According to the above equilibrium constants ($\log K_1$ to $\log K_5$) (Sillen et. al., 1964), the distribution of tungstate ions was calculated as a function of pH, as shown in **Fig. 6**. This result indicated that the tungstate ions existed as the anionic species in the wide pH range. Therefore, amines would be effective to selectively extract these ions.

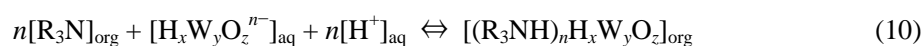
3.3 Ion exchange

The time dependence of the ion exchange is shown in **Fig. 7**. The saturated leaching solution including **W(VI)** and **Co(II)** indicates pH=7.55 and this pH range is difficult to selectively extract

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2 **W(VI)** and **Co(II)** by solvent extraction process. As shown in Fig. 7, the ion exchange is smoothly
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4 proceeded to the reaction: $R-SO_3H + Li^+ \rightarrow R-SO_3Li + H^+$. The alternation of pH was roughly
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6 proportional to the time of ion exchange. Then, as shown in Fig. 5, the complexation state of
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8 **W(VI)** ion is relatively dependent on the pH in an aqueous phase. Therefore, the aqueous phase
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10 with different pH conditions using the next solvent extraction was controlled by the time of ion
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12 exchange.

13 14 15 16 17 3.4 Extraction behavior of **W(VI)** and **Co(II)**

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19 The extraction behavior of **W(VI)** and **Co(II)** for $[R_3N]/[P_{2225}][NTf_2]$ or $[R_3N]/\text{kerosene}$ system,
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21 $R=(CH_2)_7CH_3$ in a wide pH range is shown in **Figs. 8(a)** or **8(b)**, respectively. In the case of the
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23 $[R_3N]/[P_{2225}][NTf_2]$ system, the extraction percentage (E) of **W(VI)** and **Co(II)** was >95% and <2.5%
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25 at pH = 1.0, respectively. This result indicated that W was selectively extracted at pH = 1.0 by the
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27 $[R_3N]/[P_{2225}][NTf_2]$ system. In addition, the extraction of **W(VI)** was dependent on the pH of the
28
29 aqueous phase. This extraction tendency was consistent with previous results (Carvalho et. al.,
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31 1991, Coca et. al., 1990). Regarding **W(VI)** extraction, the **ion association** process can be
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33 expressed as follows:
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38 where x , y , z , and n are the stoichiometric coefficients related to equation (10) and are highly
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40 dependent on the pH (Kim T. K. et. al., 1968). From Fig. 6, for pH = 1.0–4.5, pH = 4.5–7.0, pH =
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42 6.5–8.5 and pH = 8.5–10.0 in the aqueous phase, $[H_xW_yO_z^{n-}]$ could be expressed as $[H_3W_6O_{21}^{3-}]$ (x
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44 = 3, $y = 6$, $z = 21$, $n = 3$); $[HW_6O_{21}^{5-}]$ ($x = 1$, $y = 6$, $z = 21$, $n = 5$); $[W_6O_{21}^{6-}]$ ($x = 0$, $y = 6$, $z = 21$, $n =$
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46 6); and $[WO_4^{2-}]$ ($x = 0$, $y = 1$, $z = 4$, $n = 2$), respectively. This reaction also indicated that the
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48 extraction yield of **W(VI)** rapidly decreased with increasing pH. Moreover, the UV-Vis spectrum
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50 for $[H_xW_yO_z^{n-}]$ or $[(R_3NH)_nH_xW_yO_z]$ was measured in aqueous or organic phase. As shown in **Fig.**
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52 **9**, the shoulder peak at around 260 nm was observed in aqueous phase including $[H_xW_yO_z^{n-}]$. This
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2 result was consistent with the reference (O. Glemser et. al., 1965). On the other hand, the sharp
3 peak at around 322 nm was observed in the organic phase. We conjectured that this peak would be
4 related with the extracted $[(R_3NH)_nH_xW_yO_z]$ complex. The separation factor of W/Co in
5 $[R_3N]/[P_{2225}][NTf_2]$ or $[R_3N]/\text{kerosene}$ system was summarized in **Table 3**. As shown in Table 3,
6 the separation factor of W/Co in $[R_3N]/[P_{2225}][NTf_2]$ system is relatively larger than that in
7 $[R_3N]/\text{kerosene}$. As a result, the IL with high dielectric constant would be useful for the separation
8 of **W(VI)** and **Co(II)** for the comparison of the conventional organic solvent. Moreover, the
9 neutralization of the acidic solution after solvent extraction of **W(VI)** did not produce any detectable
10 precipitate.

11 After the removal of **W(VI)** by solvent extraction (I), the extraction behavior and slope analysis
12 of **Co(II)** by PC-88A is shown in **Figs. 10(a)** and **10(b)**, respectively. From the slope analysis, the
13 slope between $\log D$ and pH was 1.90, which indicated that the stoichiometry ratio of **Co(II)**:PC-88A
14 was 1:2. PC-88A is usually thought to be a weak organic acid that can extract metallic ions by
15 cation exchange reactions. The equilibrium for the extraction of **Co(II)** from the acidic medium
16 using PC-88A can be generalized as follows (Jayachandran et. al., 1999):



18 where $HL = (H_{17}C_8)P(OC_8H_{17})O(OH)$ and $(HL)_2 =$ dimeric form of PC-88A in the organic phase. It
19 is generally accepted that PC-88A is dimeric in low-polarity solvents (Marcus et. al., 1969). The
20 extraction yield of **Co(II)** increased with increasing pH and the extraction percentage was >95% at
21 $pH > 4.3$.

22 3.5 Reuse of organic solvent for extraction-electrodeposition

23 Finally, we investigated the reuse of the **W(VI)** in $[R_3N]/[P_{2225}][NTf_2]$, $R=(CH_2)_7CH_3$ solvent
24 for continuous solvent extraction and stripping. A series of results for solvent extraction and
25 stripping over five cycles was summarized in **Table 4**. In the 1st–5th cycles of the solvent
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2 extraction process, the extraction percentage of W(VI) with [R₃N]/[P₂₂₂₅][NTf₂] was maintained to
3 be high (90.8–97.6%). On the other hand, NaOH (0.5-1.0 mol/L) NH₃ (1.0 mol/L) base media
4 were found most successful reagents, although acid medium was unsuccessful due to the stability of
5 W(VI) complex with back extraction media. Then, NH₃ solution was preferred to NaOH solution,
6 because it was easier to produce ammonium paratungstate (APT), which is usually the final form
7 required by the tungsten industry. This result indicated that the extraction efficiency of the TOA
8 extractant was high, and [R₃N]/[P₂₂₂₅][NTf₂] could repeatedly be used for extraction-stripping
9 process.
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21 4. Conclusion

22 We demonstrated a novel hydrometallurgical process to effectively separate W and Co from
23 WC-Co hard metal. This process involved the following steps: pretreatment, leaching, ion
24 exchange, and two-step solvent extraction (I and II) using ionic liquids (ILs). First, the AlCrN film
25 coating was completely removed from the WC-Co hard metal surface by leaching in a
26 H₂SO₄–H₃PO₄ mixed acid system. Then, oxidization of the WC-Co hard metal was conducted at
27 1173 K for 10 h to form WO₃ and CoWO₄ powders, as confirmed by XRD. After the oxidization
28 process, the leaching reaction $WO_3 + 2LiOH \rightarrow WO_4^{2-} + 2Li^+ + H_2O$ proceeded and the
29 stoichiometry of WO₃:LiOH was 1:2.1, which was consistent with that of the leaching reaction. It
30 was beneficial to exchange H⁺ and Li⁺ in the leaching solution by a cation exchange resin after the
31 leaching process.
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45 A two-step solvent extraction process using ILs was employed to separate W(VI) and Co(II).
46 For solvent extraction (I), the IL [P₂₂₂₅][NTf₂] with TOA as the extractant selectively separated
47 W(VI). The extraction mechanism of W(VI) using the [R₃N]/[P₂₂₂₅][NTf₂], R=(CH₂)₇CH₃ system
48 was based on the ion association reaction $n[R_3N]_{org} + [H_xW_yO_z]_{aq} + n[H^+]_{aq} \Leftrightarrow$
49 $[(R_3NH)_nH_xW_yO_z]_{org}$. For solvent extraction (II), the PC-88A/[P₂₂₂₅][NTf₂] system was used to
50 extract Co(II). Based on the slope analysis, the extraction mechanism was revealed to be based on
51 the cation exchange reaction $[Co^{2+}]_{aq} + 2[(HL)_2]_{org} \Leftrightarrow [CoL_2 \cdot 2HL]_{org} + 2[H^+]_{aq}$. A novel
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2 hydrometallurgical process was allowed us to conclude that it was effective to separate W(VI) and
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4 Co(II) from WC-Co hard metal wastes by leaching, ion exchange and solvent extraction with
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6 $[R_3N]/[P_{2225}][NTf_2]$ system, $R=(CH_2)_7CH_3$. Finally, the reuse availability of W(VI) in
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8 $[R_3N]/[P_{2225}][NTf_2]$ solvent was investigated by continuous extraction and stripping process. In the
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10 1st–5th cycles on solvent extraction, the extraction percentage of W(VI) kept high performance
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12 (90.8–97.6%). Then, NaOH (0.5-1.0 mol/L) NH_3 (1.0 mol/L) base media was maintained high
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14 value (80.1-90.2%). This series of experimental results allowed us to conclude that
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16 $[R_3N]/[P_{2225}][NTf_2]$ solvent can be recycled from solvent extraction and stripping process.
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Caption of Figures

Fig. 1 A novel hydrometallurgical process using ionic liquid for the separation of **W(VI)** and **Co(II)** from WC-Co hard metal wastes.

Fig. 2 Molecular structure of (A) triethyl-pentyl-phosphonium cation (P_{2225}^+) and (B) bis(trifluoro methyl-sulfonyl)amide anion (NTf_2^-).

Fig. 3 SEM image of (a) AlCrN coating film on WC-Co hard metal wastes and (b) WC-Co hard metal wastes after removal of AlCrN coating film.

Fig. 4 XRD profile of WC-Co hard metal wastes and oxidized WC-Co sample at 1173 K for 10 h.

Fig. 5 Leaching behavior of **W(VI)** from oxidized WC-Co sample in 0.1 mol/L LiOH at 343 K for 19h.

●: W leached, □: pH

Fig. 6 Relationship between distribution of various tungstate ions and pH calculated by equilibration constants from $\log K_1$ to $\log K_5$.

Red line: $[H_3W_6O_{21}^{3-}]$, orange line: $[HW_6O_{21}^{5-}]$, green line: $[W_6O_{21}^{6-}]$, blue line: $[WO_4^{2-}]$ and purple line: $[HWO_4^-]$, $[H_2WO_4]$

Fig. 7 Relationship between the time of ion exchange and pH in aqueous phase.

Fig. 8 Extraction behavior of **W(VI)** and **Co(II)** (a) $[P_{2225}][NTf_2]$ and (b) kerosene by solvent extraction on $[R_3N]/[P_{2225}][NTf_2]$, $R=(CH_2)_7CH_3$ system after ion exchange. red circle: **W(VI)** for aqueous phase including $[H_3W_6O_{21}^{3-}]$, brown circle: **W(VI)** for aqueous phase including $[HW_6O_{21}^{5-}]$, rectangle: **Co(II)**

Fig. 9 UV-Vis spectrum for each **W(VI)** complex in aqueous or organic phase.

solid line: $[H_xW_yO_z^{n-}]$ in aqueous phase, dotted line: extracted $[(R_3NH)_nH_xW_yO_z]$ in organic phase

Fig. 10 (a) Extraction behavior of **Co(II)** by solvent extraction on PC-88A/ $[P_{2225}][NTf_2]$ system

and (b) slope analysis after removal of W(VI).

Fig.1

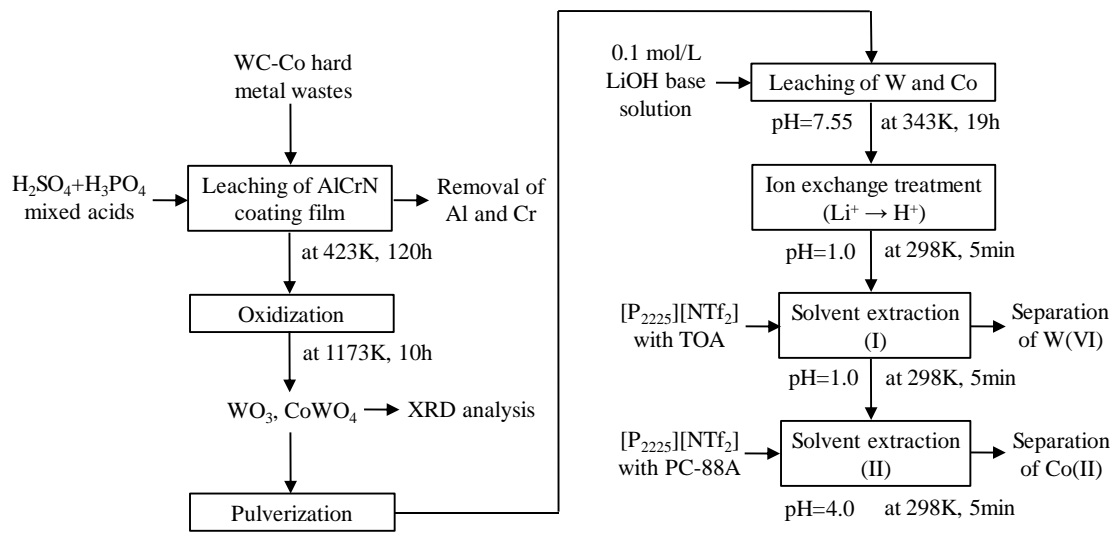
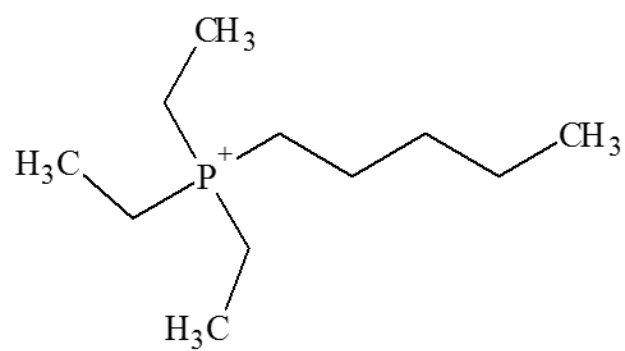


Fig. 2

(A)



(B)

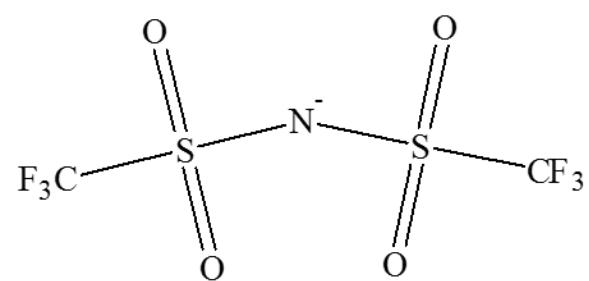
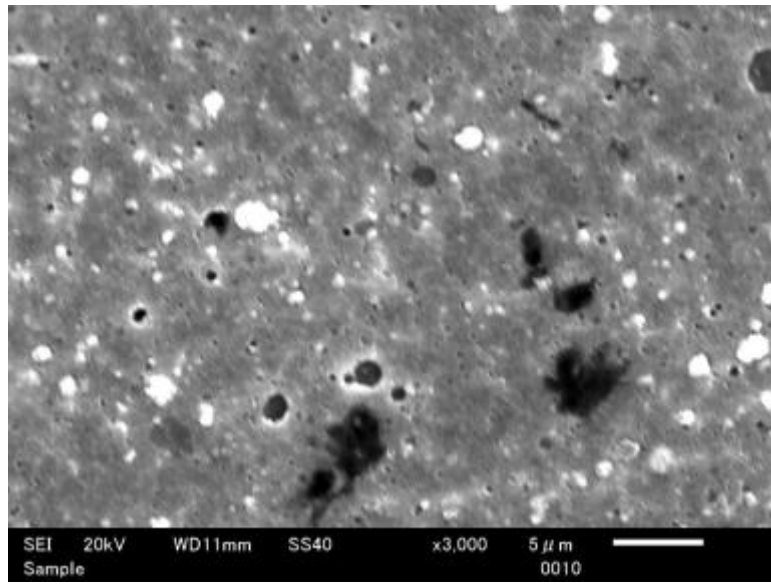
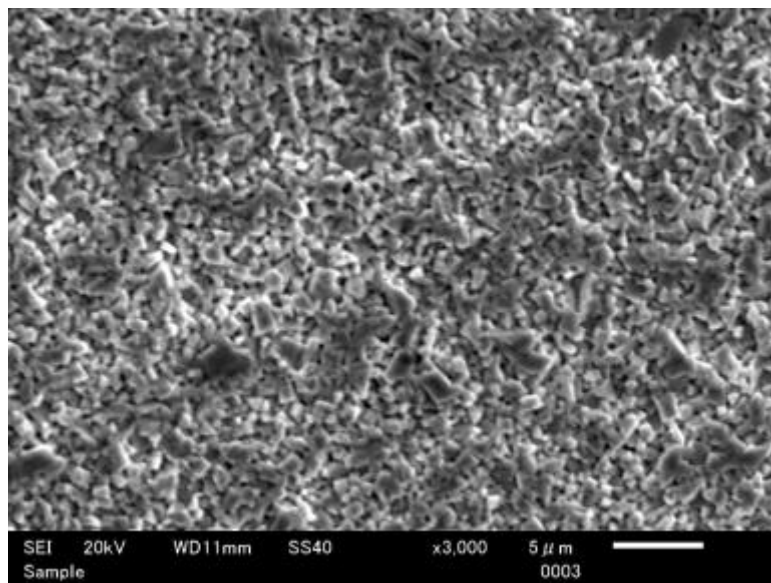


Fig. 3



(a) AlCrN coating film on WC-Co hard metal



(b) WC-Co hard metal after removal of AlCrN coating film

Fig. 4

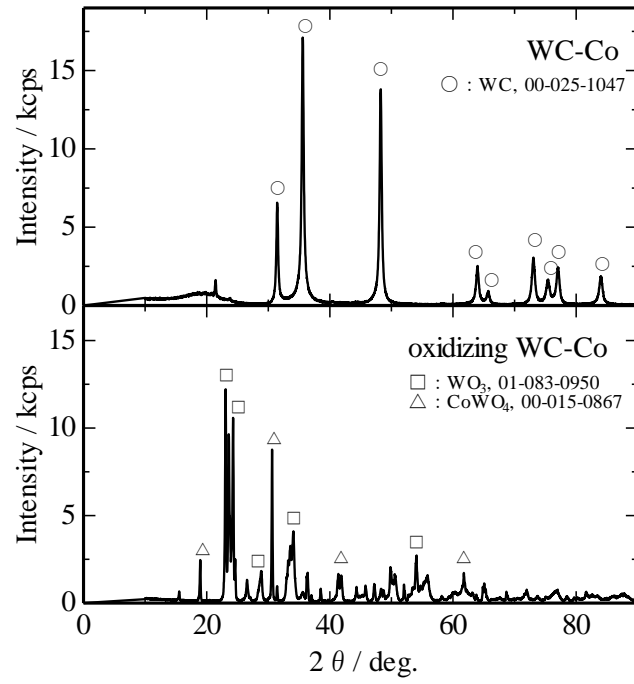


Fig. 5

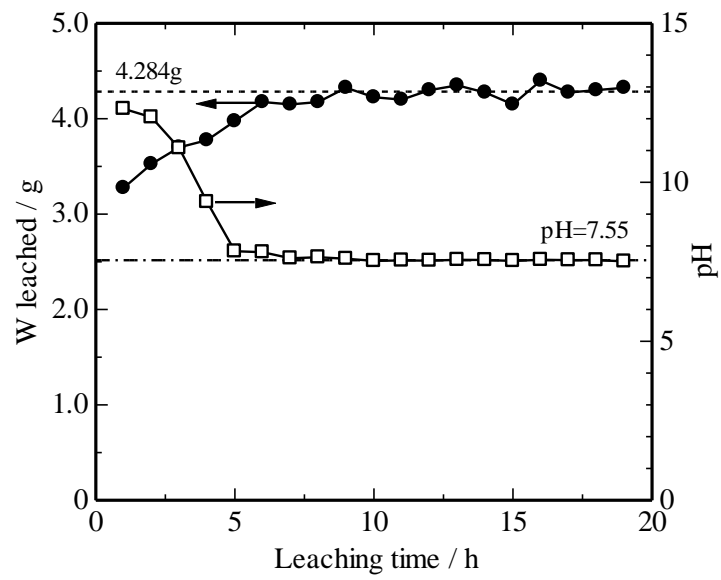


Fig. 6

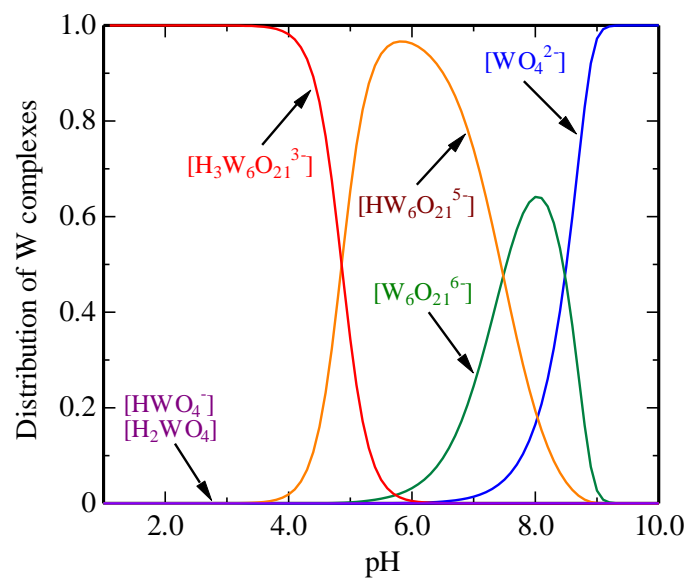


Fig. 7

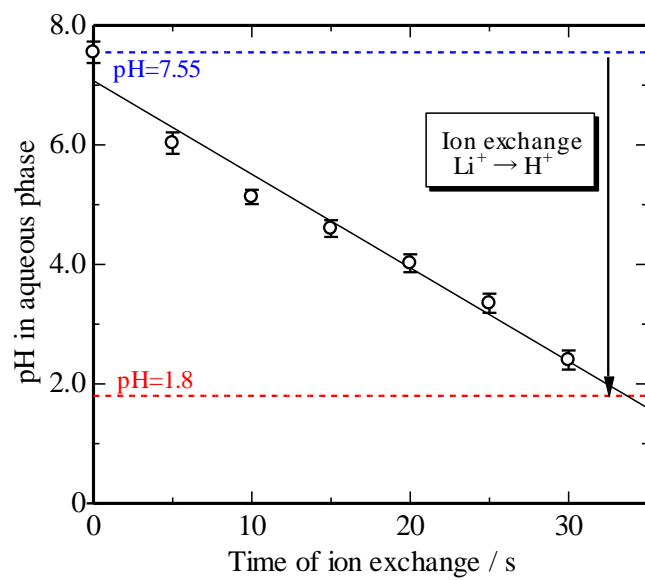


Fig. 8

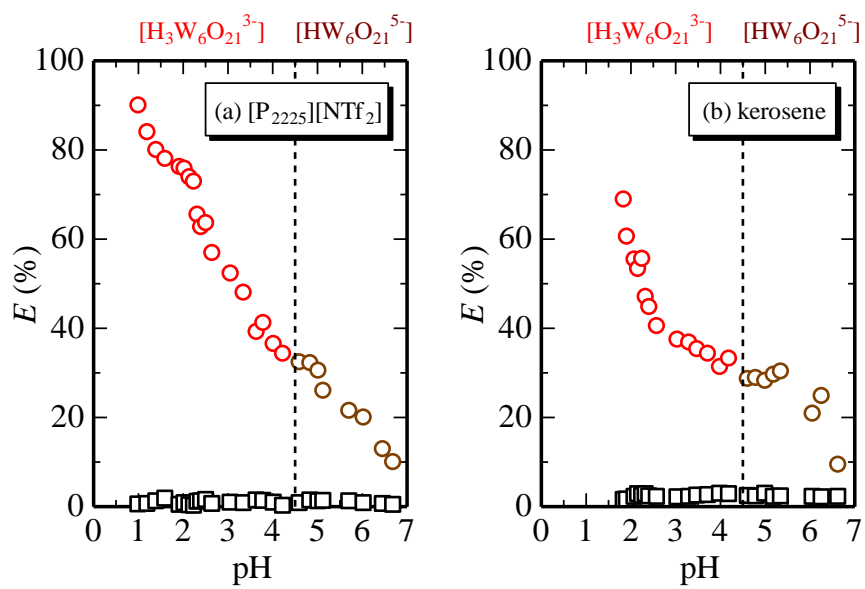


Fig. 9

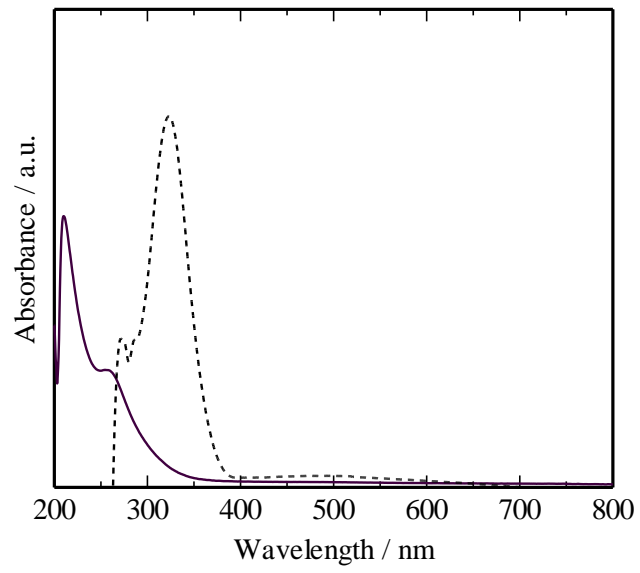


Fig.10

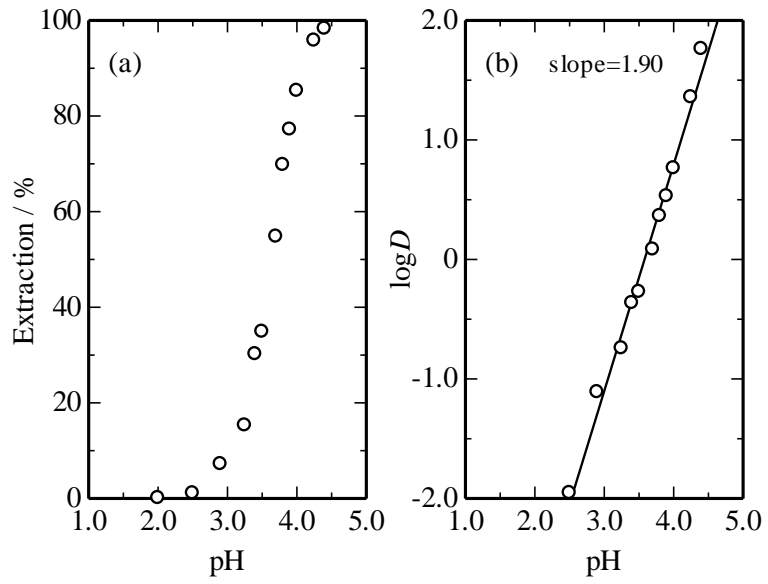


Table 1 Weight composition (wt.%) of AlCrN coating film and WC-Co hard metal by EDX analysis

	Al	Si	Ti	Cr	Co	Y	W
AlCrN coating film	47.67	0.10	0.11	51.72	0.13	0.08	0.18
WC-Co hard metal	0.09	3.05	0.55	0.03	0.47	0.85	94.96

Table 2 Polytungstates and their relation to the pH of the aqueous medium.

pH	Ionic species	<i>y/n</i>
1.0-4.5	[H ₃ W ₆ O ₂₁ ³⁻] (pseudo meta-tungstate)	2.0
4.5-7.0	[HW ₆ O ₂₁ ⁵⁻] (para-tungstate)	1.2
6.5-8.5	[W ₆ O ₂₁ ⁶⁻]	1.0
8.5-10.0	[WO ₄ ²⁻]	0.5

Table 3 Separation factor of **W(VI)** and **Co(II)** for [R₃N]/[P₂₂₂₅][NTf₂] or [R₃N]/kerosene system,
R=(CH₂)₇CH₃.

pH	W/Co in [P ₂₂₂₅][NTf ₂]	pH	W/Co in kerosene
1.92	797.2	1.91	135.0
2.32	170.7	2.33	44.1
3.35	114.5	3.30	37.0
4.02	63.3	3.99	21.8
5.02	36.1	5.00	18.8
6.03	31.0	6.06	16.8
6.69	27.7	6.63	6.6

Table 4 A series of results of W(VI) for solvent extraction and stripping process at fifth cycles.

No.	Solvent extraction	Stripping			
	[R ₃ N]/[P ₂₂₂₅]/[NTf ₂] <i>E</i> /(%)	Molarity (mol/L)	HCl <i>E</i> /(%)	NH ₃ <i>E</i> /(%)	NaOH <i>E</i> /(%)
1 st	97.6	0.5	29.8	61.4	89.8
		1.0	19.1	85.3	86.7
		1.5	13.2	74.2	75.1
		3.0	12.1	51.6	71.2
2 nd	94.8	0.5	18.2	69.2	81.6
		1.0	13.8	86.8	84.3
		1.5	12.5	73.6	75.4
		3.0	10.6	41.5	70.2
3 rd	93.2	0.5	16.1	68.9	80.3
		1.0	12.4	87.2	82.6
		1.5	10.3	77.8	71.6
		3.0	9.6	35.6	69.8
4 th	91.6	0.5	13.2	70.3	81.8
		1.0	11.6	89.2	80.9
		1.5	7.8	78.4	70.4
		3.0	8.2	40.6	65.2
5 th	90.8	0.5	12.6	73.4	80.4
		1.0	10.3	90.2	80.1
		1.5	6.9	74.1	65.8
		3.0	7.1	32.8	62.4