

Article

Leaching Behavior of Al, Co and W from the Al-Alloying Treated WC-Co Tool as a New Recycling Process for WC Hard Scrap

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Abstract: The Al-alloying treated tungsten carbide (WC)-Co tool was subjected to grinding using a jaw crusher and planetary mill followed by three wet chemical treatment steps to establish an effective recycling process for WC scraps, especially those generated as bulky and hard scrap. This alloyed WC tool was readily ground to a powder of 1 mm or less and divided into two portions that were 150 μm in size. The wet chemical treatments enabled us to recover W to 69.44% from the under-sized 150 μm and also obtain WC powders from the over-sized 150 μm with a high purity of 98.9% or more.

Keywords: WC-Co tool; Al-alloying treatment; wet chemical treatment; recovery of W; pure WC powder

1. Introduction

Tungsten carbide (WC) is a major industrial material that is used in cutting tools (including drilling tools), drawing and extrusion dies, nozzles, seals and many other applications. It has required properties, such as a high hardness, toughness, chemical inertness, and resistance to deformation. To increase these properties, other refractory carbides, such as TiC and TaC, are frequently combined with WC alloys along with a metal binder or cementing agent, typically cobalt (Co), that holds the hard carbide grains together in a dense composite structure [1–11].

Recycling research and the industrialization of cemented carbides has steadily increased in recent years due to the increasing cost of raw materials, increased scarcity of the world's tungsten reserves, and strict energy conservation regulations. Typically, these recycling methods are subdivided into two groups. One is named the direct recycling method, which involves the separation (or breaking apart) of the binder metal and carbide skeleton, leaving a finely divided carbide matrix behind with the binder material. The other is named the indirect recycling method, which involves chemical modification methods that convert carbides into different forms, such as oxides. Typical direct method examples [12–14] include the zinc-melting and cold-stream methods, while indirect methods tend to make use of acids, electrochemistry or chemical modification techniques [15–18]. Although there are many studies on effective and economical recycling of tungsten in cemented carbide tools, the most basic and critical factor is how to break down scrap pieces into powders, which may cause severe equipment wear and require a long grinding time due to the abrasive nature of the cutting tool materials.

To easily pulverize scrap, zinc-melting and high-temperature oxidation methods [19,20] have been proposed and used as an industrial procedure in WC recycling. However, each approach has some drawbacks. In the case of the zinc-melting method, which uses molten zinc to penetrate the binder layer and forms a molten alloy with binder metals, evaporation and elimination of zinc must be performed

repeatedly. This is an energy-intensive process that requires a long time and a high temperature. Also, it is difficult and complicated to adjust the conditions for controlling zinc-evaporation in the absence of oxygen. With the high-temperature oxidation method, the WC scrap is treated for a long time over 12 h at 1000 °C or higher in a pure oxygen atmosphere because the oxidation of WC proceeds slowly in oxygen. For this reason, an Al-alloying treatment was recently attempted, enabling us to grind the WC scrap by forming intermetallic compounds and oxides between the scrap and aluminum [21,22]. However, there are few studies on the recovery of valuable components from Al-alloyed scrap and there is a paucity of information on the properties of treated WC powder.

The main purpose of this research is to provide information and optimal conditions on effective and economic recycling processes of WC-Co hard metal scrap treated with an Al alloying treatment.

2. Experimental

2.1. Preparation of the Starting Powder by Pulverization of a WC-Co Cutting Tool

Virgin WC-Co cutting tools (insert-tip type, A&S Carbide cutting Co., Ltd., Chengdu, China) were used for Al-melting treatment, and their properties are summarized in Table 1. Al-melting was performed at 1350 °C for 1 h in an atmosphere environment after aluminum (Al) was mixed with the cutting tool with an Al to cutting tool ratio of 15 wt%.

Table 1. Properties of the tungsten carbide (WC)-Co cutting tool used in the Al-alloying method.

Grade	UF10	ISO range	K20-K50
Composition	WC 90%, Co 10%	Grain size of WC	~1 µm (submicron)
Density(g/cm³)	14.45	Shape	Square shape (length: 10 mm, thickness: 3 mm)

Pulverization of the Al-alloyed tools was performed using a jaw crusher (BICO Ltd., Burbank, CA, USA) and planetary mill. The primary crushing was conducted to break down to “~5 mm” with an open setting with a width of 100 mm and gap of 5 mm between the two plates in the lower (outlet) part. Successively, the crushed material was ground using a planetary mill (Pulverisette 5, Fritsch GmbH, Idar-Oberstein, Germany), and its conditions were as follows: 250 g of the crushed material was placed into each stainless pot ($\Phi = 100$ mm, H = 80 mm) with 2 stainless balls that were 45 mm in diameter and subjected to grinding in air at 200 rpm for 20 min. By grinding at these conditions, the product could be screened with a #16 sieve (aperture size: 1 mm) for a complete pass. The procedure of making starting materials is summarized in Figure 1.

2.2. Starting Materials and Their Characterization

The ground was classified into one of two portions, under-(U150) and over-sized portions (O150), by sieving with a #100 sieve (aperture size: 150 µm), and the samples were separately preserved in a gas-tight plastic container and then used as the starting materials in this study. The weight ratio of O150 and U150 was surveyed at 26.5:73.5. Starting materials were characterized by high-resolution X-ray diffraction (HRXRD) analysis (X’pert-pro MPD, PANalytical, Almelo, The Netherlands) using CuK α radiation ($\lambda = 1.5406$ Å) to identify the phases formed by the Al-melting treatment of the cutting tools. Moreover, the particle size distribution and morphology, including the surface chemical properties, were measured with a particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., Malvern, UK) and field emission scanning electron microscope (FESEM-EDS, S-4300, Hitachi, Tokyo, Japan), respectively.

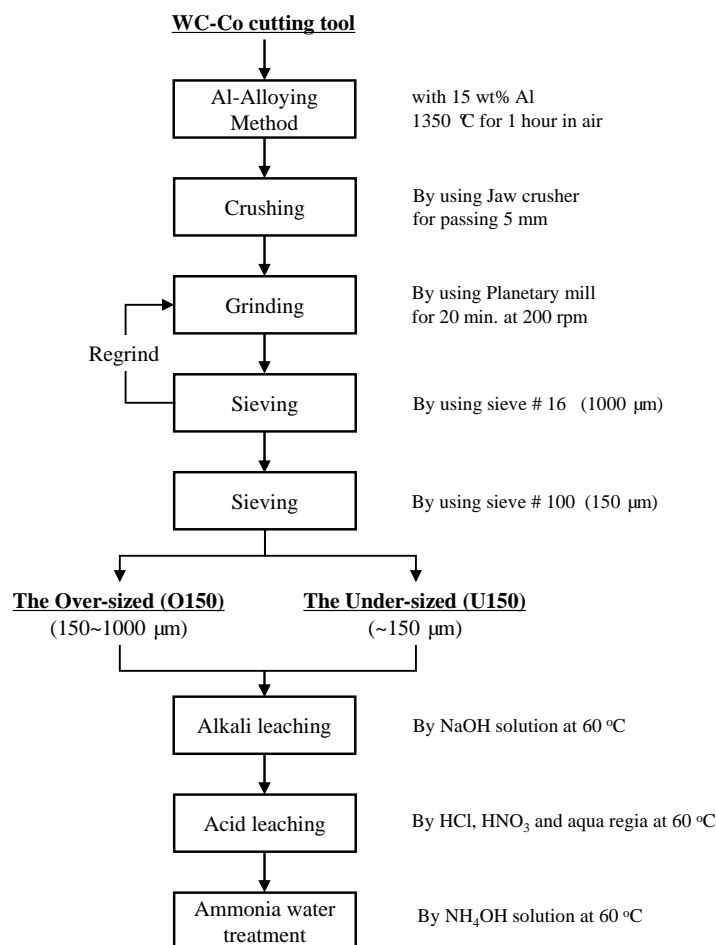


Figure 1. The preparation procedure of starting materials and the flow chart of the recovery experiment used in this research.

3. Results and Discussion

3.1. Characterization of the Starting Powders of the Al-Alloyed WC-Co Cutting Tools

Characteristic analysis for the classified samples, by size, was performed to acquire information about the Al-alloyed WC-Co tool and determine the leaching procedure to effectively recovering valuables. Figure 1 shows the XRD patterns of the starting samples that were pulverized and classified by size using #16 and #100 sieves for the Al-alloyed WC-Co tools O150 and U150. The mean sizes of O150 and U150 were 448.2 μm and 5.5 μm, respectively. As shown in Figure 2, there are a large number of differences in their compositions. In the case of O150 (Figure 2a), the peaks of only two materials are observed in the pattern, that is, peaks of WC are primarily present and those of Al₄W are marginally detected. For the pattern of U150 (Figure 2b), various compounds can be observed, such as CoWO₄, Al₂O₃, Al₂(WO₄)₃, Al₄W, and WC. The main peaks are those of WC in both patterns, and the intensity is higher in the pattern of U150 than in that of O150. This indicates that the oxides may be broken down more easily than the other ingredients. Namely, it is implied that the Al-alloyed WC consists of intermetallic, oxide compounds as well as unreacted WC; subsequently, the oxides with lower hardness may be shifted to U150 through pulverization and size classification with a cut-off of 150 μm.

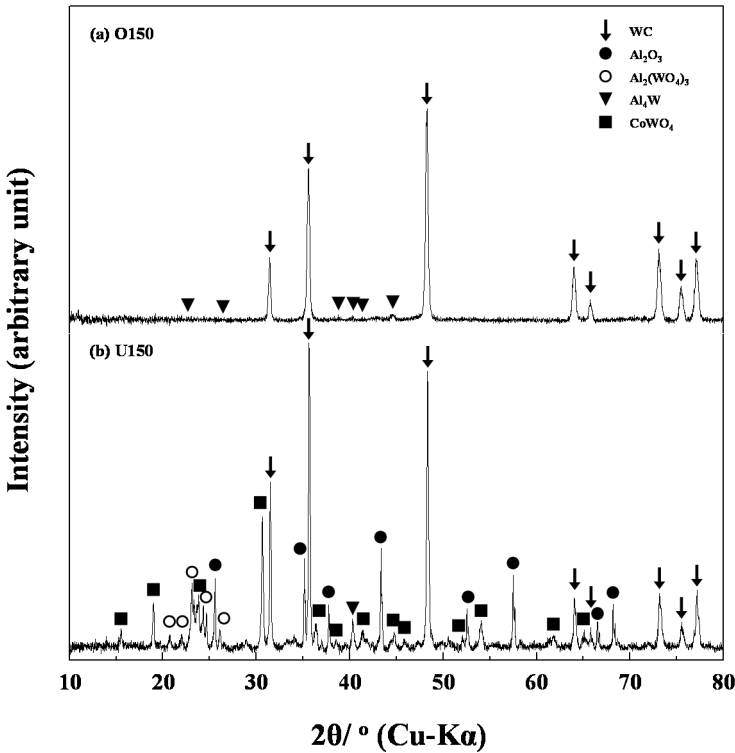


Figure 2. X-ray diffraction (XRD) patterns of the Al- alloyed WC-Co tool classified by size of 150 μm ((a) O150, (b) U150).

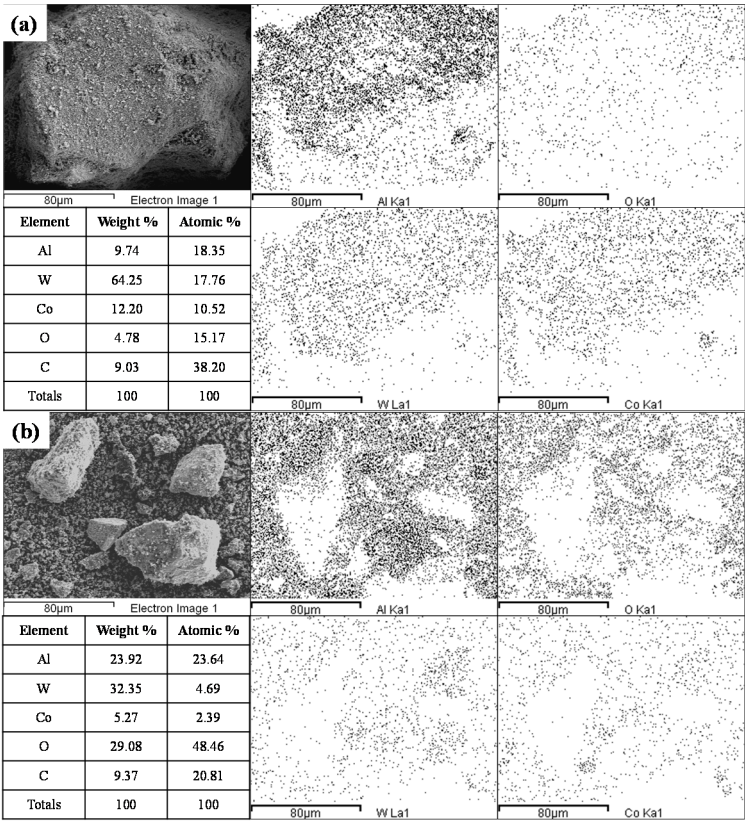


Figure 3. Results of scanning electron microscopy/energy dispersive X-ray spectrometry (SEM-EDS) analysis for two starting powders ((a) O150, (b) U150).

To check the morphology and surface chemical property of the two starting samples, SEM/EDS (scanning electron microscopy/energy dispersive X-ray spectrometry) analysis was performed, as shown in Figure 3. Powders in both samples are also an irregular polyhedral shape, which can be observed in the ground product. Moreover, the Al and O levels are higher in U150, while those of W, Co, and C are higher in O150. These results are in accordance with the result of XRD analysis (Figure 2). Finally, the chemical compositions of U150 and O150 were analyzed using ICP after these were completely dissolved through the chemical digestion method. This method was carried out in two steps, (1) alkali fusion with the mixture of Na_2NO_3 and NaOH at 900 °C for 2 h, (2) acid digestion in HF at 90 °C. Especially, acid digestion was conducted repeatedly until no residue remained. These results are summarized in Table 2.

Table 2. Chemical composition of the starting materials, O150 and U150 (unit: wt%).

O150		U150	
W	72.00	W	46.71
Co	7.48	Co	6.33
Al	6.61	Al	19.03

3.2. Leaching Treatment for the Al-Alloyed WC-Co Powder

A 500 mL, 3-inlet pyrex flask that was placed on the heating mantle was used to conduct the leaching treatment for the Al-alloyed WC powder. This flask was equipped with a PID temperature controller and a variable-speed stirrer. The leachate volume, slurry density, temperature and stirring speed were fixed at 200 mL, 10 g/L, 60 °C, and 400 rpm, respectively. To acquire more accurate data for leachability, leaching was performed three times under the same conditions, and the leachability was calculated according to the following equation:

$$\text{Leachability of M (\%)} = \frac{\text{M content (A)}}{\text{M content (A)} + \text{M content (B)}} \times 100 \quad (1)$$

where M denotes the target metal (Al, Co, and W). The content of M (A) is the M mass calculated from the M concentration in the leached solution, and the M content (B) represents the M mass in the leached residue after complete dissolution.

Leaching treatment proceeded in a successive three-step process as follows: (1) alkali leaching with NaOH; (2) acid leaching with aqua regia, HNO_3 , and HCl; and (3) ammonia solution treatment. The purposes of the first and second steps were to investigate the leaching behavior of Al, and Co, respectively. The treatment with ammonia solution was performed for the dissolution of tungstic acid, which was formed in the process of acid leaching.

3.2.1. Alkali Leaching with NaOH

Figure 4 shows the leaching trend of Al and W according to the NaOH concentration and leaching time. In the case of leaching for O150 (a), W was rarely dissolved (maximum leachability: 1.85%, 133 ppm) in all conditions. Meanwhile, Al dissolution increased sharply until 30 min and was almost complete within 120 min., irrespective of the NaOH concentration from 1 to 6 M (maximum leachability: 96.9%, 843 ppm). For U150, the yield of W was considerably enhanced to 17.3% (810 ppm) and that of Al reached 45.0% (856 ppm) at most. In summary, the leachability of Al in O150 was higher than that in U150, while W from O150 was seldom dissolved compared to that for U150. These results can be explained by the comparison of their composition and components, as shown in Figure 2 and Table 2. In the case of O150, only two components, WC and Al_4W , were detected in the pattern and could be scarcely dissolved in an alkali solution. Also, the Al content in O150 was nearly three-fold lower than that for U150. While, as for U150, the Al content was relatively higher and WC was the main component, while there were also various oxides, such as CoWO_4 , $\text{Al}_2(\text{WO}_4)_3$ and Al_2O_3 ,

that might be leached in the NaOH solution. As a result, the leachability of Al in O150 was far superior to that in U150, although the leached mass of Al was similar in each setting, such as 843 ppm for O150 and 856 ppm for U150. Moreover, the unreacted WC and intermetallic component Al_4W was rarely extracted by alkali leaching in 6 M of NaOH at 60 °C. On the other hand, W from oxides, such as CoWO_4 , $\text{Al}_2(\text{WO}_4)_3$, and Al_2O_3 , might be comparatively dissolved at the same leaching conditions.

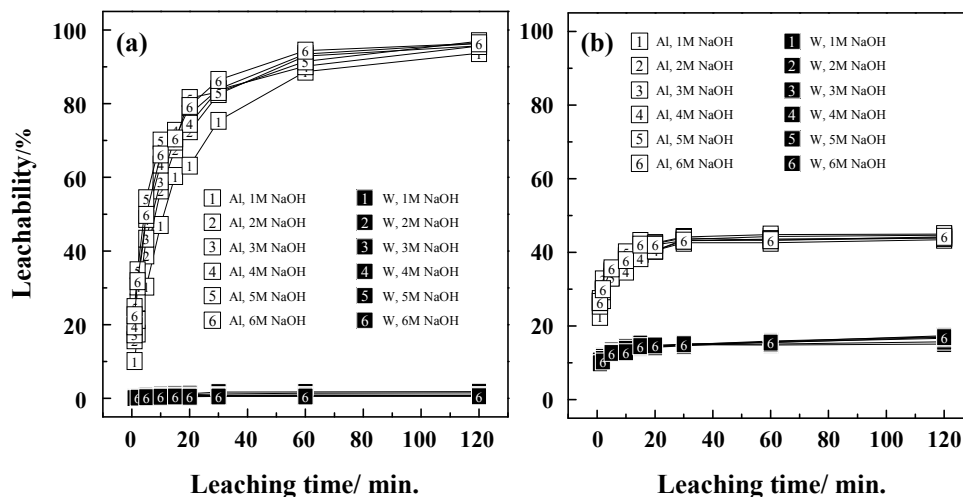


Figure 4. Effect of the NaOH concentration and duration time on the dissolution of Al and W in alkali leaching treatment for (a) O150 and (b) U150 (pulp density: 10 g/L, temperature: 60 °C, stirring speed: 400 rpm).

3.2.2. Acid Leaching

As previously mentioned, the trend of alkali leaching was not greatly influenced by the NaOH concentration in the range of 1 to 6 M; thus, the residue leached by 6 M NaOH was fixed as an object in the acid leaching treatment. To prepare the acid leaching sample, the leached residue was repeatedly washed at room temperature three times using distilled water with the purpose of eliminating the basicity at the surface, and it was then dried at 105 °C for 2 h in succession. To provide more information about the leaching tendency of the alkali-leached residue in acid, three types of acid solution (aqua regia, 4 M HCl, and 4 M HNO_3) were used in this step, while other variables were fixed (10 g/L pulp density, 60 °C, and 400 rpm stirring speed).

In the case of the O150 residue (Figure 5a), the leaching rate of Al was slightly different; it had a sort of acid solution, but the component of Al that remained in the residue was completely extracted within 120 min, regardless of the type of acid solution. Meanwhile, the remaining Al in the alkali-leaching residue of U150 (Figure 5b) can be slightly dissolved over 120 min (3.9% in HNO_3 , 3.63% in HCl, and 8.4% in aqua regia). These results might be explained in the components, as shown in Figure 2 and Table 2. The content and ingredient composition of Al were different between O150 and U150. Al in O150 existed as Al_4W at a lower level (6.61%) than that of U150 (19.03%) and was mainly in the form of Al_2O_3 . The dissolution of Al_4W may be easier than that of Al_2O_3 during the acid and alkali leaching treatment.

Meanwhile, in all types of leachate used in this study, the leaching of Co from the residue of O150 proceeded quickly in the initial period for 20 min and slightly increased (90.2%) in HNO_3 ; it was 94.3% in HCl and 100% in aqua regia. With the residue of U150, Co could be nearly completely extracted in all three types of leachate (99.1% in HNO_3 ; 100% in HCl and aqua regia). To summarize these results, Co could be extracted under all of the experimental conditions at a level of more than 94.3% from Al-alloyed WC-Co scrap after alkali leaching treatment with 6 M NaOH; one exception was the case of 4 M HNO_3 with leaching for the O150 residue (Co leachability of 90.2%).

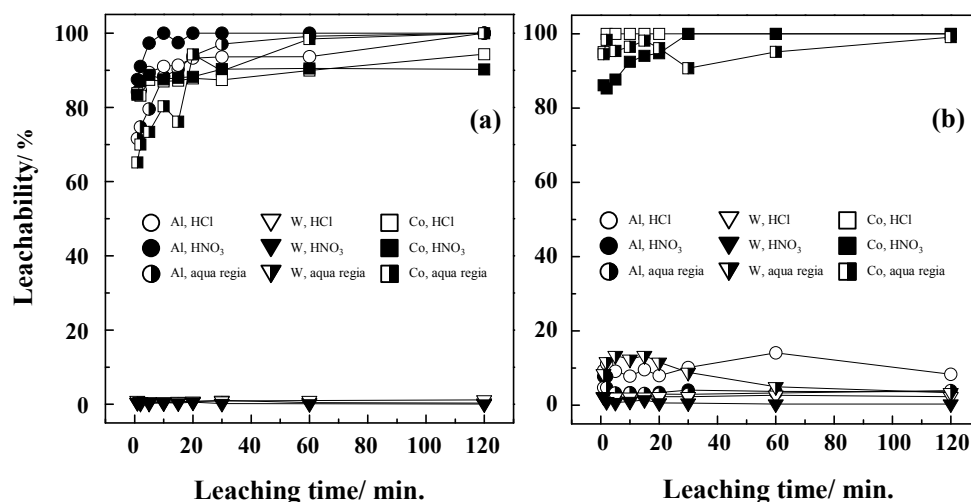
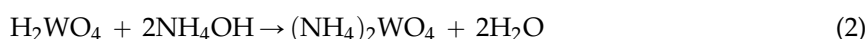


Figure 5. Variation of the leachability of Al, Co, and W in the three types of acid solution for the alkali-leached residue of (a) O150 and (b) U150 (pulp density: 10 g/L, temperature: 60 °C, stirring speed: 400 rpm).

On the other hand, W could be seldom dissolved, and its yield was less than 3.4% after 120 min in all leachates, although the leachability of W from U150 was somewhat higher than that from O150. The low leachability of W might be from the formation of tungstic acid, which was insoluble in an acidic solution. To dissolve the tungstic acid formed in the acid-leaching residue, treatment with a 4 M ammonia solution was performed in succession. In this way, the leachability of W could sufficiently explain the results of ammonia leaching, as shown in Figure 6. The dissolution of tungstic acid in ammonia solution can be expressed as follows [20]:



As shown in Figure 6, only the W component was detected in the solution that was treated with O150, whereas Al was extracted concurrently by ammonia solution treatment for U150 as well as W. For the dissolved W in ammonia solution, the leachability from the residue of U150 was much higher than that of O150. In addition, the extraction of W was somewhat different with the change in the acidic leachates, but the dissolution in all cases was so fast that it was complete within 30 min. The maximum leachabilities of W from both O150 and U150 were higher, as follows: from the residue of O150 (aqua regia: 14.48%, HNO_3 : 12.48%, and HCl: 1.78%) and from the residue of U150 (aqua regia: 54.65%, HNO_3 : 40.81%, and HCl: 11.79%). The order of the leachabilities of Al from U150 differed as follows: 17.54% in HCl, 12.38% in HNO_3 , and 12.19% in aqua regia. The lack of detection of Al in the solution might indicate the absence of Al in the residue of O150, as shown in Figure 6a. Additionally, the leachability of W in an ammonia solution implies the degree of tungstic acid formation, which resulted in the reaction between WC and acidic leachates. As stated above, this reactivity in all residues was superior for aqua regia, HNO_3 , and HCl, although there were some differences in the leachability of each residue. The higher leachability of W in U150 might be attributed to the size of WC in the residue. A summary of the cumulative leachability of W is follows; for O150 (HCl: 4.88%, HNO_3 : 15.84%, and aqua regia: 18.85%) and for U150 (HCl: 30.76%, HNO_3 : 51.21% and aqua regia: 69.44%). To calculate the purity of WC in the final residues of O150, the residues were completely dissolved using chemical digestion. As the result, the WC purities were estimated to be 99.6% (HCl), 98.9% (HNO_3) and 99.7% (aqua regia).

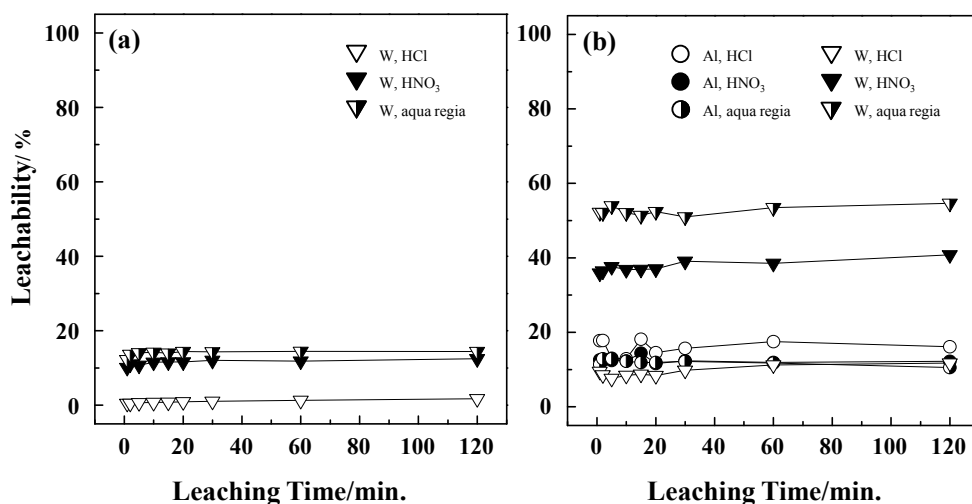


Figure 6. Extraction of Al and W from the acid leaching residue of (a) O150 and (b) U150 by ammonia solution treatment (NH_4OH conc.: 4 M, pulp density: 50 g/L, temperature: 60 °C, stirring speed: 400 rpm).

As a result, the 3-step, successive wet chemical treatment enables us to obtain considerably pure WC powder from O150 of the Al-alloyed WC-Co powder as well as, to dissolve the W component up to approximately 69.44% maximally from U150 of the Al-alloyed powder.

4. Conclusions

With two starting powders prepared from the Al-alloyed WC-Co tool, three steps of wet chemical treatments were successively performed to provide information on the effective recycling process of hard metal scrap. The following conclusions can be made based on the experimental results.

Through Al-alloying treatment, the WC-Co tool was converted to the easy-pulverizable state, which consisted of Al_4W , CoWO_4 , $\text{Al}_2(\text{WO}_4)_3$, and Al_2O_3 as well as WC. This alloyed WC tool was readily ground to powder that was 1 mm or less by crushing by a jaw crusher and grinding by a planetary mill at only 200 rpm for 20 min.

With the ground WC tool, two starting materials were prepared using a #100 sieve, such as under-sized (U150) and over-sized of 150 μm (O150) sieves. There were many differences in the compositions of the two starting materials, which are summarized as follows: O150 consisted of unreacted WC and intermetallic (Al_4W), whereas U150 consisted of several oxides (CoWO_4 , $\text{Al}_2(\text{WO}_4)_3$, and Al_2O_3) as well as unreacted WC.

As for alkali leaching to Al and W components, the effect of the NaOH concentration was ineffective in the range of 1 to 6 M. Within 120 min, Al in O150 could be virtually leached to the extent of 93.7% or higher. Moreover, the leachabilities of W from U150 were much higher than those from O150, and these results might be from their composition and components.

By acid leaching with 3 types of leachates after alkali leaching with 6 M NaOH, Co could be dissolved in both the O150 (minimum leachability: 90.49% by HNO_3) and U150 residues (minimum leachability: 99.12% by HNO_3). Also, Al in the O150 residue was completely leached, regardless of the acid type. With respect to the leachability of W, the reacted W in acid leaching might be easily formed as tungstic acid (H_2WO_4), which is insoluble in an acidic solution. For this reason, an ammonia solution treatment was performed on the acid leaching residues.

The cumulative maximal leachabilities of W were 18.85% for O150 and 69.44% for U150. Moreover, high purity WC powders could be obtained from O150 as the final residues after three successive steps of wet chemical treatment.

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Conflicts of Interest: The authors declare no conflict of interest.

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