

Development of High-Efficiency Recycling Technology for Tungsten

Chemical state analysis of tungsten during ion exchange in collection system

Achievements

- Development of a method of collecting **tungsten*** using an **ion exchange method****
- Analysis of the change in the chemical state of tungsten during ion exchange
- Optimization of adsorption and elution conditions to enable the highly efficient collection of tungsten throughout the entire process (95%) and to reduce energy consumption by 40%

R&D facility: Sumitomo Electric Industries, Ltd.

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***Tungsten** is a rare metal with the chemical symbol W and the highest melting point of all metals. Tungsten production is small, and its extraction is locally distributed in China. Tungsten carbide is used as the principal component of carbide tools because of its high hardness.

****Ion exchange method:** A sample is placed in a column filled with an ion exchange resin, and the target substance is adsorbed onto the resin. Then, a buffer solution used for elution is introduced into the column to separate the adsorbed substance from the resin and obtain the target substance.

Used carbide tools and tips containing tungsten



Used carbide tips



Tools for urban development



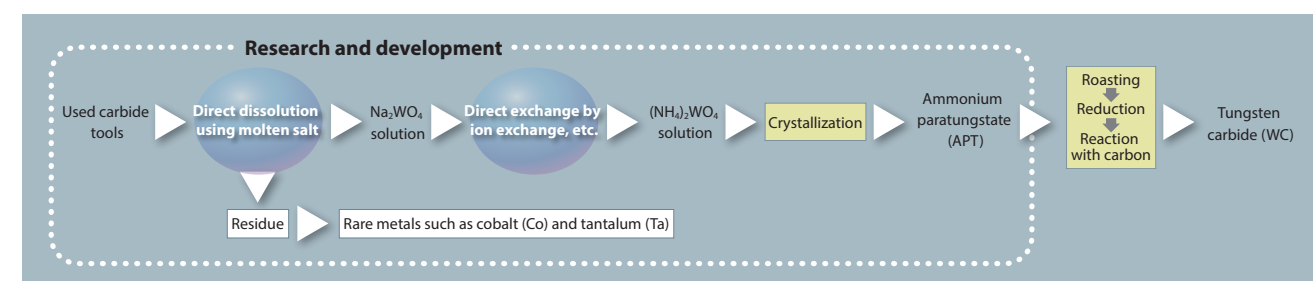
Used drills and endmills



Wear-resistant tools

Recycling process of tungsten

Used carbide tools are dissolved in molten salt to obtain a Na_2WO_4 solution. The solution is introduced into an ion exchange resin to collect tungsten ions in the $(\text{NH}_4)_2\text{WO}_4$ solution, which is then heated and condensed so that it crystallizes as ammonium paratungstate (APT). APT is oxidized by roasting to obtain WO_3 , which is then reduced to tungsten. The obtained tungsten is reacted with carbon to form the reusable tungsten carbide (WC).



Role of SPring-8

Background

Demand for tungsten is increasing, whereas its natural abundance is small. To help ensure a stable supply of tungsten, techniques for efficiently collecting and recycling tungsten from used carbide tools and tips are necessary.

Among the various methods for collecting tungsten, a method using an ion exchange column, which can be performed in a small-scale system compared with conventional methods, is expected to reduce the environmental load of tungsten recycling. To achieve efficient ion exchange, tungsten should be fully adsorbed onto an ion exchange resin and be completely eluted. In practice, however, tungsten crystals precipitate, clogging the column, and preventing the complete elution of tungsten. This has remained a long-standing problem.

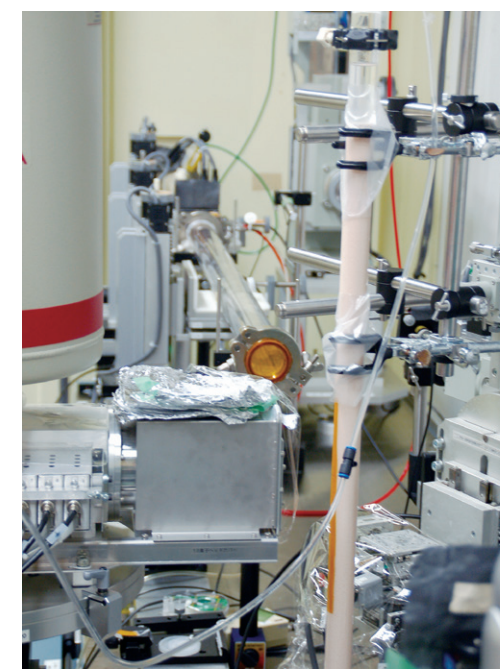
Results

X-ray absorption fine structure (XAFS) measurement using SPring-8 synchrotron radiation can reveal the electronic state and chemical structure of substances in a sample. Three tungsten ion species, WO_4^{2-} , $\text{HW}_6\text{O}_{21}^{5-}$, and $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$, were introduced separately into the ion exchange column, where they were adsorbed onto the ion exchange resin and eluted. XAFS measurement revealed that some of the adsorbed $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$ ions, which contain the most tungsten atoms of the three species, still remained in the resin. Detailed analysis clarified that the ions were partly decomposed into the other two ion species and these three ion species remained in the resin at a certain proportion.

From the above result, optimal conditions for the adsorption and elution of tungsten were determined, thus improving the collection efficiency of tungsten.

XAFS measurement at SPring-8

The long thin tube is the ion exchange column. Synchrotron radiation is irradiated onto the orange film.



XAFS measurement results for adsorbed ions remaining in resin during ion exchange of $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$

White circles represent measured values. The spectra of three tungsten ion species (WO_4^{2-} , orange; $\text{HW}_6\text{O}_{21}^{5-}$, blue; $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$, green) are used as references in the analysis. When the percentages of WO_4^{2-} , $\text{HW}_6\text{O}_{21}^{5-}$, and $\text{H}_2\text{W}_{12}\text{O}_{40}^{6-}$ are 32, 13, and 55%, respectively, the spectrum of the adsorbed ions remaining in the resin fits the white circles. From this result, the percentages of the remaining ion species in the resin were obtained.

