

Industrialization of Tungsten Recovering from Used Cemented Carbide Tools

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Tungsten is a chief ingredient of hardmetal materials. Since its sources are concentrated in China, the supply of tungsten is highly volatile, and therefore, a reduced dependence on China would stabilize the hardmetal business. In view of this, the Sumitomo Electric Group focused on recycling tungsten from used hardmetal tools. The group developed an efficient recycling technology with a low environmental load, and industrialized the technology in a joint research project. Despite various challenges that came up on the way to industrialization, the group succeeded in establishing the technology as a business. This paper mainly describes the developed technology, which reduces toxic emissions and removes impurities. Our goal now is to recycle even low grade tungsten scrap, most of which is currently being disposed, and thus contribute to a more efficient use of rare metals.

Keywords: cemented carbide, tungsten, recycling, resource saving

1. Introduction

Tungsten (W) is a rare metal known to have properties such as a high melting point, high specific gravity, high hardness, a low coefficient of thermal expansion, high thermal conductivity, and radiation shielding capabilities. Owing to these features, this metal is used in a wide range of applications.

Tungsten is principally used in the carbide tool industry in the form of WC, which is the main raw material of cemented carbide. Cemented carbide is used in many industries including automotive, aircraft, electronics, civil engineering, and construction, as cutting, mining and civil engineering tools, as well as dies and heat-resistant members.

One characteristic of tungsten demand breakdown by country/region and application (Fig. 1) is that carbide tools account for approximately 61% on a global average. Notably, in Japan, carbide tools account for a higher percentage of the tungsten demand than the global average, at 76%.

While tungsten is such an important resource, as described above, the amount of tungsten ore deposits is unevenly distributed on the earth, approximately 60% of which is in China. In 2014, China accounted for 83%

of the world's tungsten production. In 2012, the Ministry of Economy, Trade and Industry designated tungsten as one of five important minerals, the others being Ta, Nd, Dy and Co, from the perspectives of industrial importance and supply stability.

According to 2013 data from the International Tungsten Industry Association (ITIA), the recycling rate was 50% in Europe and the United States in contrast to 30% in Japan. To improve the tungsten recycling rate in Japan, it is efficient to use scrap cemented carbide because the tungsten content in cemented carbide is more than 80%, which is higher than in other uses.

Stable procurement of raw materials is the key for Sumitomo Electric in ensuring the stable production of carbide tools in its hardmetal business. To meet this challenge, we developed a technology and established recycling routes for obtaining W from used cemented carbide on a commercial basis, which is detailed in this paper.

2. Types of Scrap Cemented Carbide

Scrap cemented carbide is roughly classified into hard solid scrap and soft powder scrap. The former includes cutting inserts, drills, and dies, while the latter, produced at cemented carbide material and carbide tool manufacturers, include W and WC powders with a high W content, as well as sludge with a relatively low W content, produced from cemented carbide grinding and polishing processes.

Currently, several tungsten recycling and refining companies operate in Japan. Collection of scrap W is on an increasing trend. However, the amount of recycled W has not increased. The shipping of carbide tools for 2014 increased from 2013 by approximately 13%, while on the other hand the drain of scrap W to overseas countries has also increased.

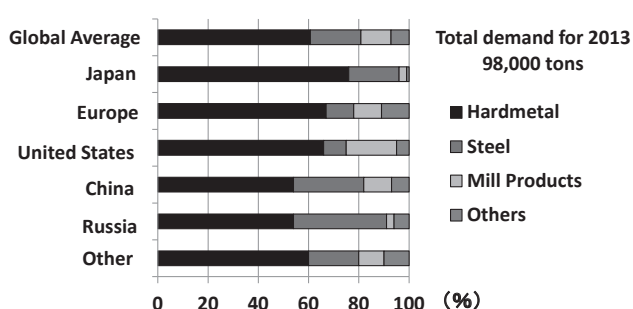


Fig. 1. Demand for tungsten by country/region and application

3. Features of Newly Developed Tungsten Recycling Technology

Carbide tool recycling methods are roughly classified into two types: direct and indirect. The direct method processes hard scrap into powder with the chemical composition intact. The indirect method chemically dissolves hard or soft scrap and subsequently collects individual components separately.

Typical recycling techniques include the zinc treatment process (direct) and the oxidation-wet chemical treatment process (indirect). Other techniques have emerged in the past; however, they are rarely used today due to the limited applications of the recycled powder, cost, and poor productivity.

The zinc treatment process is advantageous in that it consumes small amounts of chemicals and energy, requires a small capital investment, and is feasible for small-scale industrial production. However, this process allows the chemical composition of scrap to remain in the recycled products, necessitating proper screening when collecting scrap. The cost of screening is a burden that undermines the advantageous cost of the process. Moreover, in this process, cutting tools, which account for a high percentage of tungsten-based products, are recycled along with the coating components, problematically degrading the quality of the recycled material.

In comparison, the oxidation-wet chemical treatment process is comparable to ore refining in resulting quality, with no specific limitations to applications. However, this process uses large amounts of chemicals during purification. Furthermore, as an additional problem, this process requires large-scale treatment facilities, hence a large capital investment.

The Sumitomo Electric Group began to use the zinc treatment process in the 1980s. Additionally, Sumitomo Electric has commenced a new efficient recycling business based on the oxidation-wet chemical treatment process. The following description provides an overview of the new recycling technology.

Participating in the national project "Development of a Highly Efficient Rare Metal Recovery System" organized by Japan Oil, Gas and Metals National Corporation (JOGMEC), Sumitomo Electric Industries, Ltd., Sumitomo Electric Hardmetal Corporation, A.L.M.T. Corporation, and Nagoya University, in a joint research program, have developed a new recycling technology specializing in the treatment of scrap cemented carbide with high efficiency even on a small scale. This technology was commercialized in 2011 by A.L.M.T. Tungsten Corporation. Figure 2 outlines the process.

Key points in the program were the development of a molten-salt dissolution technique for efficiently dissolving hard scrap, and the development of an ion-exchange technique that enables high-efficiency exchange and removal of impurities.

3-1 Molten-salt dissolution technique

The basic technique used to extract high-purity WO_3 from scrap cemented carbide is to convert a sodium tungstate (Na_2WO_4) solution into an ammonium tungstate [$(NH_4)_2WO_4$] solution, concentrate this solution to allow ammonium paratungstate [APT ($(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$)] to

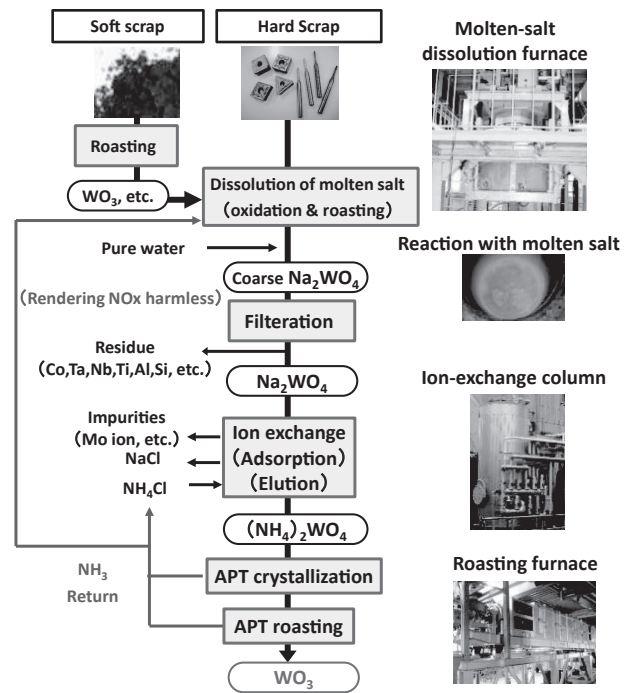


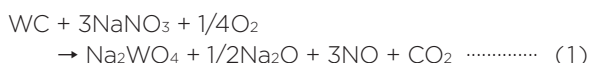
Fig. 2. Outline of new oxidation-wet chemical treatment process

crystallize, and roast obtained APT. First of all, with this technique, it is necessary to oxidize WC in the process, soft scrap can be oxidized more easily than hard scrap. It is difficult to oxidize hard scrap to its interior. For full oxidation, hard scrap needs to be peeled of its oxide layers and reoxidized repeatedly. Thus the basic technique is substantially problematic because it requires a large amount of energy and labor, and a high treatment cost.

The newly developed technique was designed to dissolve strongly oxidative sodium nitrate ($NaNO_3$) together with scrap, oxidize and at the same time have the scrap react with Na, and produce Na_2WO_4 . Using this technique, it is possible to oxidize hard scrap to the interior. By aqueous dissolution of the product, a Na_2WO_4 solution can be obtained, eliminating the need for an alkaline extraction process.

The aforementioned reaction is exothermic, generating a large amount of heat. While appropriate from an energy-saving perspective, it needs to meet the challenge of controlling the fast reaction. Soft scrap is not suitable for this treatment because its large surface area results in explosive acceleration of the reaction. Moreover, the emission gas from this reaction contains toxic nitrogen oxides (NO_x), necessitating thorough measures to treat the emission gas. To control the reaction, we opted to feed $NaNO_3$ powder at a low constant rate to a largely excessive amount of hard scrap. In addition, we developed a technique for making full use of $NaNO_3$. After dissolving WC through the reaction expressed by Eq. (1), part of $NaNO_3$ remains as Na_2O , which is weakly oxidative. By adding WO_3 as roasted

soft scrap to the melt obtained by Eq. (1), WO_3 is converted to Na_2WO_4 through the reaction expressed by Eq. (2).



One problem of this process is that the treatment of scrap made of fine grained cemented carbide results in the production of hexavalent chromium because the process uses a trace amount of Cr as an additive (grain growth retarder) and a strong oxidizing agent. As a measure to counter this problem, we developed a technique of adding suitable amounts of W, WC, and C powders as a reducing agent to the molten salt.

Furthermore, to treat NO_x gases produced in this process, we applied a catalyst-based technique in use at thermal power plants. Nitrogen oxide gases produced are NO and NO_2 , which are unstable; in other words, they tend to change their forms. The aforementioned technique uses a detector to detect NO_x gases, allows them to react with a suitable amount of ammonia gas, and decomposes NO_x gases into harmless nitrogen gas (N_2) and water vapor (H_2O), as expressed by Eqs. (3) and (4).



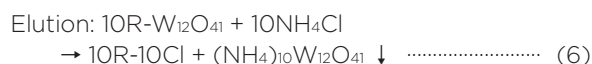
3-2 Ion-exchange technique

One purpose of ion exchange is to obtain a $(NH_4)_2WO_4$ solution by allowing WO_4^{2-} ions contained in a Na_2WO_4 solution to adsorb on anion exchange resin and to elute the ions with an ammonium salt such as ammonium chloride (NH_4Cl). Another purpose is to remove impurities from aqueous solution through molten salt dissolution. Exploiting differences in the adsorption selectivity of different ion species, we developed a process of converting coarse Na_2WO_4 to pure $(NH_4)_2WO_4$ with smaller equipment than that used in the conventional method in a resource-saving manner without environmental burden.

Ion exchange occurs when an aqueous solution passes through a column filled with ion-exchange resin. The ion species fed to the ion-exchange resin adsorbs on the resin through an ion-exchange reaction with the ion species originally binding with the resin. Dominant factors in ion exchange reaction include the concentration of the ion species contained in the aqueous solution, the adsorption selectivity, and the ion size.

The amount of W that a unit volume of ion-exchange resin can adsorb (exchange capacity) depends on the valence and the amount of W of the ion species containing W. The newly developed technique is particularly highly efficient, allowing about a three times higher amount of W than by the conventional method to be adsorbed through a reaction expressed by Eq. (5) owing to the use of tungsten polyacid ions.

The next step is to elute the adsorbed tungsten polyacid ions. Passing NH_4Cl through the column for this purpose would cause APT to deposit through the reaction expressed by Eq. (6), resulting in clogging of the column piping. To avoid this it is necessary to maintain the basicity of the aqueous solution and decompose the tungsten polyacid ions eluted through the reaction expressed by Eq. (7). Our solution to this challenge was to pass a mixed solution that contained high-concentration NH_3 ($NH_3 + NH_4Cl$) through the resin column at a high flow rate. The result was about three times higher efficiency in ion exchange than the conventional technique without depositing ATP.



*R: Denotes an ion exchanger of ion-exchange resin.

4. Commercialization of New Oxidation-Wet Chemical Treatment Process

In line with the aforementioned key development factors, we installed demonstration mass-production facilities at A.L.M.T. Corporation and verified the effectiveness of the facilities. While refining businesses generally use large-scale facilities, we have established a new chemical treatment process that is, even though small, highly efficient, environmentally friendly and safety-minded. Later, the process was commercialized at A.L.M.T. Tungsten Corporation. However, other problems emerged, preventing the facilities from operating as planned and necessitating additional development efforts, which are described below.

In the research and development phase, hard scrap of clearly known composition and soft scrap of relatively high W purity were used as raw materials. Attempts to collect and treat various types of scrap, which included various foreign bodies and impurities, revealed the necessity of establishing not only an impurity separation technique, but also operation and management procedures. Moreover, individual measures entailed increased processes and costs, necessitating efficiency improvements with regard to chemicals, consumables, and energy used within the recycling system.

4-1 Measures to counter fluidity and oil content problems in the oxidation-roasting process

After the commercialization, a huge challenge emerged. We were not hesitant to use outsourced soft scrap, which contained steel bolts and waste cloth, sludge from grinding and polishing contained grinding wheel components, water and oil. Accordingly, it was necessary to adapt the process to accommodate these materials.

One noteworthy point is that sludge was inconsistent in water content and formed lumps depending on its dryness. It therefore became necessary to improve the pulverization process for improved fluidity and oxidation performance to be exhibited when loading sludge into the roasting furnace. Figure 3 shows a schematic illustration of the soft scrap roasting furnace. Before heat treatment, dry lumps of scrap are crushed and pulverized for improved exposure to the air during heat treatment. Pulverized scrap is then loaded into the roasting furnace continuously and heated in air at approximately 700°C. Since the emission gas may sometimes have a foul odor due to its oil content, an emission gas combustor is used to render the emission gas harmless. Heat-treated powder is treated in the molten-salt dissolution furnace.

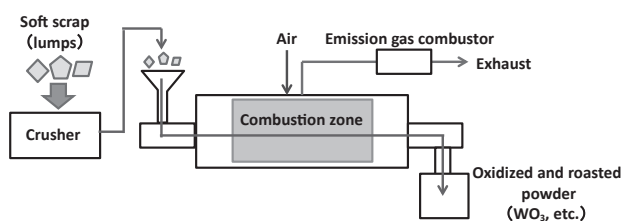


Fig. 3. Outline of soft scrap oxidation/roasting furnace

To roast scrap with an oil content, this process was found to incur the risk that oil would ignite due to excessive oil content in scrap in the roasting furnace before scrap oxidation, and that the combustion zone would expand toward the inlet, possibly burning the equipment. Therefore, arrangements were made in operation such that a cooling function was provided for the inlet zone to delay ignition, and intermittent scrap transfer was set up to prevent the spread of fire even in the event of ignition.

4-2 Anti-impurity measures and operation control for the ion-exchange process

To recycle tungsten using, as a starting material, scrap that contains many different impurities such as Al, Ca, Fe, Mo, Si and V, the purification processes that the conventional method employed were $Mg(OH)_2$ co-precipitation, which would generate a large amount of waste, and sulfurizing precipitation that would generate toxic H_2S gas. In contrast, we worked on the establishment of a precipitation process with a reduced amount of waste, a purification technique used in conjunction with ion exchange, and an operation system. However, two major problems arose: the generation of complex forms of impurity ions that were difficult to remove, and the degradation of ion-exchange resin.

Regarding the first problem of removal of impurities, in the early stage of commercialization, the product occasionally exceeded the applicable impurity concentration limits, resulting in frequent suspension of opera-

tion before solutions were devised and implemented.

Impurities are mostly removed as residues from a coarse Na_2WO_4 solution through the precipitation process, with a fraction of them remaining in the solution. Our competitors remove impurities by ion exchange with a long resin column and by virtue of adsorption selectivity. Our resin column was small and we had difficulties in removing impurities that contained Mo similar in properties to W.

Contained in cermet or used in grinding wheel dressers, Mo is inevitably contained in scrap as trace metals. Although Mo was removed basically due to its adsorption selectivity, the problem was unremoved trace amounts of Mo being contained in the product at a rate of tens of ppm. Our solution to this problem was to develop a simple procedure of quickly analyzing the Mo concentration of $(NH_4)_{10}W_{12}O_{41}$ solution collected during the process of ion exchange, to regulate the conditions of the subsequent crystallization process according to the Mo concentration, and to control the level of Mo contamination of the product at approximately 2 ppm. This technique allowed us to stabilize product quality and ensure the required level of process capability.

Moreover, the element V, used similarly to Cr as a particulate carbide grain growth retarder, was troublesome because it caused the ion-exchange resin to degrade as explained later, and after removal by precipitation resulted in a large amount of industrial waste. As a solution to this problem, we developed a technique of selectively removing V by conditioning solution properties into a form of W-V cluster ions such that the ion-exchange resin would adsorb substantially no W, yet would strongly adsorb V, followed by passing the solution through a small column designed to remove V.

In sum, we placed elements such as Mo and V, which are difficult to remove, under control and identified optimal conditions for ensuring the yield of W, which rose to approximately 97% in comparison with the initial target of 95%.

Meanwhile, because the above-described solution entailed an increase in chemical usage and additional processes, we strove to reduce the process duration. For example, $NaCl$ solution produced by the W ion adsorption process was rinsed with pure water and discharged, under control with a conductivity meter. At some times, the rinsing duration was several times longer than at other times. The cause was identified as low pure water temperatures due to seasonal influences. Waste heat generated outside the process was used to warm the pure water. The result was efficient rinsing and removal of $NaCl$ (Fig. 4).

The second problem was the deterioration of the resin. Initially, the resin was thought to remain usable semipermanently. However, it turned out that the exchange capacity would decrease due to the deterioration of the resin. While impurities are removed by using selective adsorption, a trace amount of impurities bound with W fails to be eluted from, and accumulates on, the ion-exchange resin, resulting in degradation of the resin (Fig. 5). The resin placed in the column degrades gradu-

ally from top to bottom. Hence, as a consumable-oriented measure, it is effective to replace the resin locally in view of the degree of degradation. However, in actual operation, resin replacement necessitates making changes to achieve optimal conditions. After replacement, new resin has a high exchange capacity, well adsorbing W ions as well as impurity ions. Facilitating the discharge of impurities in turn helps W to leak out. Incidentally, the adsorption of a large amount of W ions leads to the risk of APT crystallizing in the resin column during the elution process. In sum, it is desired on the one hand to make the optimal use of ion-exchange capacity for no decline in the yield, and yet on the other to remove impurities for consistent quality (Fig. 6).

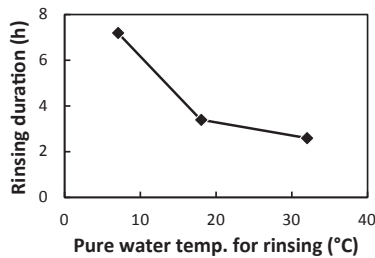


Fig. 4. Influences of rinse water temp. on Na ion rinsing duration

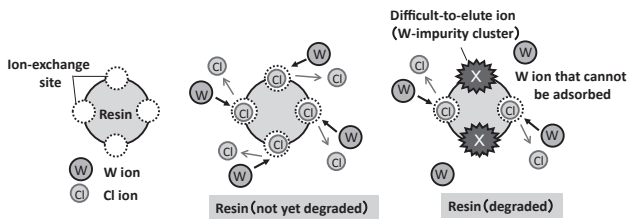


Fig. 5. Principle underlying degradation of ion-exchange resin

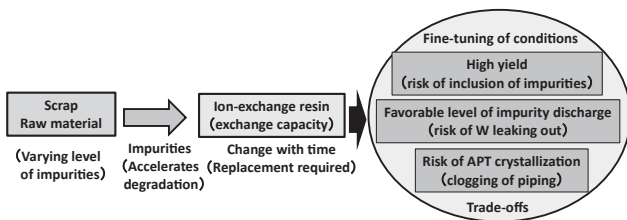


Fig. 6. Optimization of ion-exchange conditions suitable for the degree of resin degradation

Scrap that is the raw material for the recycling process varies in the level of impurities each day. Despite this, the recycling of W has been successfully commercialized through the stabilization of product quality and cost, which required a series of arrangements, including fine-tuning the process conditions suit-

able for the exchange capacity of the resin, reuse of degraded resin for impurity removal, recovery of W from degraded resin by an additional technique, and efficient use of energy.

4-3 Changes to recycling circumstances and establishment of collection routes

(1) Changes in circumstances surrounding the recycling business

Since the beginning of the tungsten recycling project, the business environment has substantially changed and the benefits of recycling have been also undergoing a change. Figure 7 shows the current trend in the tungsten market price. China's policy on tungsten has caused supply instability. In June 2011, in Europe, the London Metal Bulletin quotations for tungsten increased to 464 \$/metric ton unit. Consequently, in Japan, domestic recycling of tungsten became the focus of attention. However, in 2014, the WTO ruled against China. China's export ceiling on tungsten was removed in May 2015, resulting in a sudden drop in the market. The market price of scrap tungsten also fell. Against the backdrop of ongoing development of alternative materials to rare metals and rare metal-saving materials, concerns have arisen over the expected difficulty in stable procurement of scrap under the influence of the market.

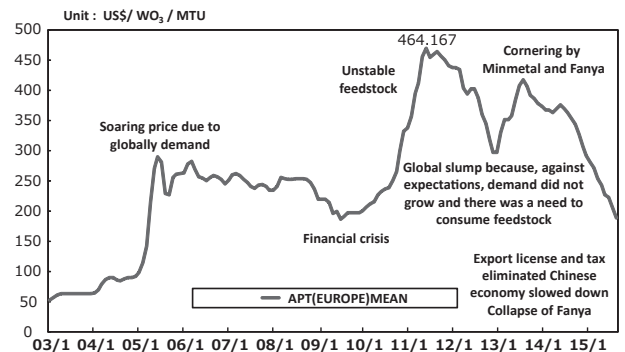


Fig. 7. International market price of tungsten (London Metal Bulletin)

The present development project started in 2005, when the tungsten price sharply increased, with the aim of ensuring the stable procurement of raw tungsten materials, and was commercialized in 2011. When the market price is high, recycled tungsten powder is substantially advantageous in terms of purchase prices over fresh tungsten powder. However, when the market price is low, the price difference between recycled and fresh tungsten powders becomes small. Consequently, for the recycling business to continue, it is necessary to process low-cost raw materials efficiently.

Moreover, it is also necessary to establish a route for collecting discarded carbide tools and sludge produced from carbide tool manufacturing processes and to develop a recycling technique for valuable Co

and Ta contained in cemented carbide, with the aim of enhancing the benefits of the recycling business.

(2) Establishment of a scrap collection route

For the recycling business to be successful, it is essential to ensure stable provision of the raw material, or scrap cemented carbide. In addition to scrap treatment technology, it is important to build analysis, control, and operation systems. Since the 1980s, Sumitomo Electric Hardmetal Corporation has been collecting scrap cement carbide from Sumitomo Electric Group companies and other companies. Sumitomo Electric Tool Net, Inc., a distributor of carbide tools, collects used tools from its customers. Collected scrap cemented carbide is gathered and screened at the Igetalloy Scrap Center. Scrap cemented carbide of known composition is recycled by the zinc treatment process. For scrap of unknown composition, we have a route established for sending it to an overseas WC powder manufacturer for conversion into WC powder.

Currently, the recycling business has incorporated a new chemical treatment process, which enables treatment of the latter unscreenable scrap. A.L.M.T. Corporation, which sells W and WC powders, also collects raw material from its customers for the new technique. Hard scrap treated as industrial waste and sludge from grinding and polishing by cemented carbide are produced in large quantities in the market. To collect these materials, we explain the need for domestic recycling of rare metal resources to participants at the Japan International Machine Tool Fair (JIMTOF) and other similar events.

Through these efforts, combining separate collection of scrap carbide products and the world's first innovative tungsten recycling technology, Sumitomo Electric in partnership with Toyota Motor Corporation established a domestic recycling system as a business ahead of other companies to recover tungsten from scrap carbide products. In 2014, the two companies won a Resource Recycling Technology and System Award for these achievements. This is believed to have promoted recycling awareness in Japan.

Furthermore, U.S.-based Niagara Refining LLC, a joint venture between Sumitomo Electric and Buffalo Tungsten, commenced a scrap recycling project along with ore refining, in an attempt to ensure the stable supply of carbide tools to our customers, and price stability.

5. Conclusion

The Sumitomo Electric Group recycles tungsten, combining and taking the respective advantages of the zinc treatment and the new chemical treatment processes. Currently, the recycled quantity in weight equals that of carbide tools distributed in Japan by Sumitomo Electric Hardmetal Corporation.

The new chemical treatment process was commercialized in 2011. Since then, we have optimized process conditions, facilitated the reuse of chemicals and energy within the recycling system, and established operation

and control methods. Consequently, the process has become industrially successful even in Japan, being implemented in a small plant commensurate with the amount of recycled scrap.

Future tasks include the development and commercialization of low-grade sludge treatment techniques in order to maximize the advantages of recycling in light of possible declines in the market price for tungsten.

6. Acknowledgments

The research on tungsten recycling was conducted as part of JOGMEC's national project "Technological Development for Recycling Tungsten and Other Material from Scrap Carbide Tools."

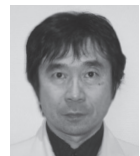
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