Development of Technologies for Recycling Cemented Carbide Scrap and Reducing Tungsten Use in Cemented Carbide Tools

Tomoyuki ISHIDA*, Takeshi ITAKURA*, Hideki MORIGUCHI and Akihiko IKEGAYA

Tungsten, the main component of cemented carbide tools, is subject to supply risk. This work considered two countermeasures: recycle and saving. For recycling, hydrometallurgy process was investigated in order to use all applications of tungsten resources. Although the hydrometallurgy process requires large-scale production facilities for cost effectiveness, we have solved the problem by developing high efficiency and low cost technique specializing for recycling cemented carbide. For tungsten saving, a composite structure of cemented carbide and cermet was developed to reduce tungsten usage. We report the cutting performance and breakage resistance of the composite structured tool.

Keywords: cemented carbide, recycle, resource saving, cermet

1. Introduction

Tungsten (W) is used as the raw material for cemented carbide alloys and special steels (high speed steels and heat resistant alloys). Taking advantage of the characteristics of tungsten, such as hardness, heat resistance, and wear resistance, it is used in cutting tools, mining and civil engineering tools, metal molds, heat resistant members, etc. Thus, wide use is made of it in machine parts and processing tools in all industrial fields including automobiles, aircrafts, electronic equipment, civil engineering, and architecture. According to the actual record of the breakdown of tungsten consumption in 2007, cemented carbide tools accounted for 66%, indicating that the percentage borne by these tools to the total consumption is high. According to the U.S. Geological Survey, the amount of minable deposits of tungsten resources is 2.9 million tons. Therefore, if the present production volume continues, the resources will be exhausted in 40 years[1]. Furthermore, tungsten resources are over-concentrated in Canada, China, and Russia. In particular, China accounts for 62% of the amount of deposits and 85% of ore production volume. The market price of tungsten rose sharply for reasons such as increased demand within China and export restrictions imposed by China. The price rose from 240 dollars/10 kg in early autumn of 2010 to 465 dollars/10 kg in July 2011, and is 400 dollars/10 kg as of May 2012, hovering at a high level. Such a situation is anticipated to continue. In order to stably manufacture cemented carbide tools in the hard metal business of our company, it is necessary to promote stable procurement of raw materials and the saving of tungsten in products. For the purpose of dealing with these matters, the authors have carried out development with regard to a technique for recycling tungsten from cemented carbide scrap generated in Japan and tungsten-saving tools by forming composite structures. The results of development are reported herein.

2. Development of Technique for Recycling Tungsten from Cemented Carbide Scrap

2-1 Conventional recycling technique and development goal

Methods of recycling tungsten from cemented carbide scrap can be broadly divided into two types: direct methods and indirect methods. A typical example of the direct methods is the zinc treatment method. This method does not use any chemicals or any water solution, and consumes little energy. Therefore, for the following reasons, among others, this method has the advantage of being realized even in small-scale recycling. However, there are restrictions on the materials to be recycled in terms of application for the following reasons: since scrap is recovered in its original composition, it is necessary to strictly select scrap; it is impossible to recycle powder scrap such as ground sludge; furthermore, since there is no purification process, purity decreases. Meanwhile, in the case of the wet chemical treatment method, which is an indirect method, the recycling process is generally incorporated into an ore refining process. This method has the advantage that there are no restrictions on cemented carbide scrap and that it is possible to obtain raw material with as high a purity as in ore refinement. However, this method suffers from the problem that large quantities of chemicals and energy are used in the purification process, resulting in waste being generated with the consequence that great environmental loads are imposed. Furthermore, there is also a disadvantage that no profitability is achieved unless production is performed using large-scale equipment. The authors aimed to resolve these problems by developing a high efficiency treatment technique specialized in cemented carbide scrap recycling.

2-2 Concept of development of recycling process

Figure 1 shows the flow of the newly developed tungsten recycling process. In order to put production on a profitable basis by means of small-scale production equipment in Japan, where strict environmental regulations are applied, it is necessary to achieve the following: (1) high
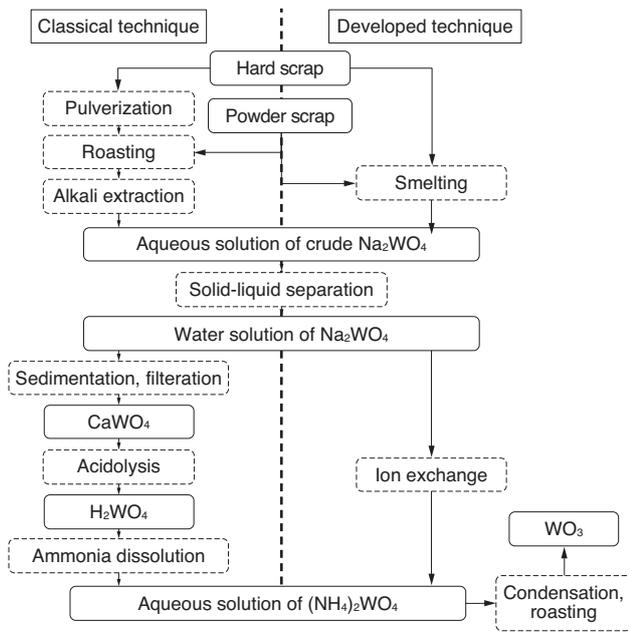
Fig. 1. Flowchart of recycling processes

Fig. 2. Molten salt solution reaction

efficiency recovery; (2) reduction in chemicals used and conservation of energy; and (3) low environmental loads. In addition to tungsten carbide (WC), which is the main component, the following substances, which are additives, are contained as impurities in cemented carbide scrap: cobalt, titanium, nickel, iron, chromium, vanadium, etc. Efforts were made to reduce treatment costs not only by achieving high efficiency in tungsten recovery but also by limiting target impurities to the elements and concentration ranges contained in cemented carbide and by specializing in recycling, thereby improving the efficiency of impurity removal. The main point where this process significantly differs from conventional techniques is that molten salt solution treatment is used to obtain an aqueous solution of Na_2WO_4 from the cemented carbide scrap and that ion exchange treatment is used to convert the aqueous solution of Na_2WO_4 into an aqueous solution of $(NH_4)_2WO_4$. In this article, these two types of treatment are described in detail.

2-3 Molten salt solution process

The purpose of the molten salt solution process is to cause the reaction of WC-Co cemented carbide alloy with $NaNO_3$, and to dissolve the generated Na_2WO_4 molten salt in water, thereby obtaining an aqueous solution of Na_2WO_4. **Figure 2** shows photos taken when the cemented carbide scrap was put into $NaNO_3$ molten salt at 720°C. Tungsten carbide, which is the main component of a cemented carbide tool, reacts with the $NaNO_3$ molten salt as shown in **Formula 1**, thereby generating Na_2WO_4 molten salt. This reaction is so fast that scrap can be melted in a highly efficient way. Furthermore, since the calorific value of the reaction is as high as 1,830 kJ/kg-WC, external heating is not required after the start of the reaction, thus saving energy. As for the solution reaction of a cemented carbide tool due to $NaNO_3$ molten salt, there was a problem in that reactivity was so high that it was difficult to control reaction. As a
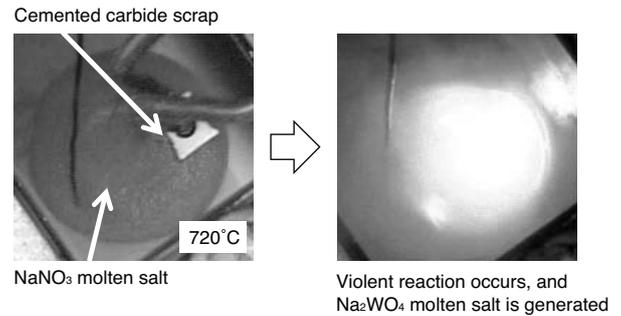
countermeasure against this problem, a method was applied in which a fixed quantity of $NaNO_3$ powder was supplied little by little to the cemented carbide scrap, enabling the reaction to be controlled for gradual scaling-up.

$$WC + 3\,NaNO_3 + 1/4O_2$$
$$\rightarrow Na_2WO_4 + 1/2Na_2O + 3NO + CO_2 \quad \cdots\cdots\cdots (1)$$
$$WC\,(powder) + Na_2CrO_4 + 5/4O_2$$
$$\rightarrow 1/2Cr_2O_3 + Na_2WO_4 + CO \quad \cdots\cdots\cdots\cdots (2)$$
$$WC\,(powder) + Na_2O + 2O_2$$
$$\rightarrow Na_2WO_4 + CO \quad \cdots\cdots\cdots\cdots\cdots (3)$$
$$WO_3\,(powder) + Na_2O \rightarrow Na_2WO_4 \quad \cdots\cdots\cdots (4)$$
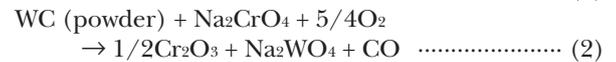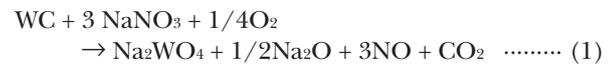
The oxidizing power of $NaNO_3$ molten salt is so strong that impurity elements contained in cemented carbide scrap, such as cobalt, titanium, tantalum, nickel, chromium, and vanadium, are also oxidized up to the maximum oxidation states. As a result of the above, it follows that, as shown in **Table 1**, chromium and vanadium change into water-soluble Na_2CrO_4 and $NaVO_3$, which then get mixed in with the aqueous solution of Na_2WO_4. Unreacted $NaNO_3$ is also water-soluble, and it is essential to remove it. In addition, for the purpose of effectively utilizing the chemicals, it is desirable to completely react the unreacted $NaNO_3$ with WC. Firstly, to make the chromium and vanadium insoluble, powder scrap, which is liable to react, is used to cause the reactions in **Formulae 1 and 2**, with the result that Na_2CrO_4 and residual $NaNO_3$ are reduced, and at the same time, Na_2WO_4 is obtained. **Figure 3** shows the amounts of powder scrap added, and Cr^{IV}, V^V, and NO^{3-} concentration changes in aqueous solution of Na_2WO_4. $NaNO_3$ and Na_2CrO_4 that remained due to the addition of powder scrap are changed into Na_2WO_4, NO, and Cr_2O_3 by

Table 1. Behavior of impurity elements during molten salt solution treatment

Additive	TiC	TaC	Co
Reaction product	$Na_8Ti_5O_{14}$	$NaTaO_3$	$NaCo_2O_4$
Rate of solution in water (%)	0	2	20
Additive	Ni	VC	Cr_3C_2
Reaction product	NiO	$NaVO_3$	Na_2CrO_4
Rate of solution in water (%)	15	70	97
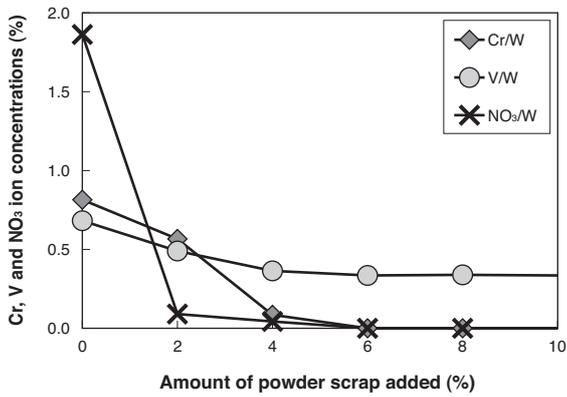
Fig. 3. Amount of powder scrap added and ion concentrations of relevant elements
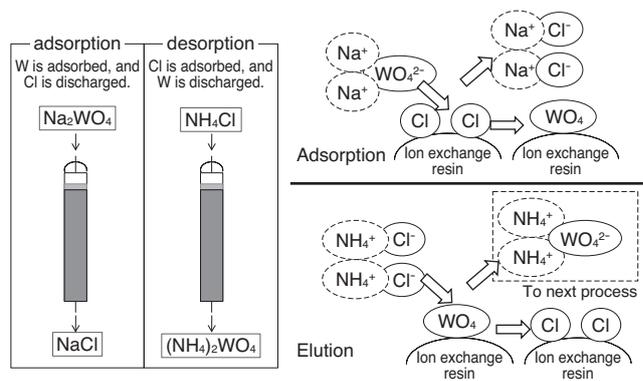
Fig. 5. Schematic diagram of ion exchange treatment
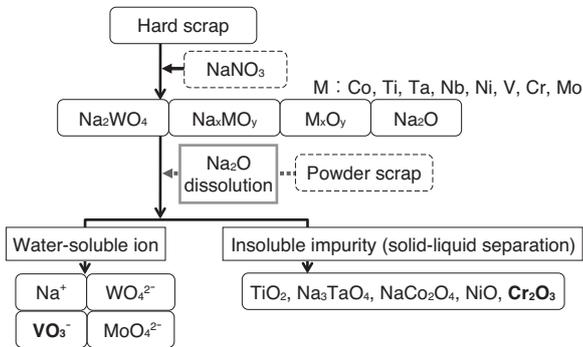
Fig. 4. Molten salt solution process and impurity behavior

the reactions of **Formulae 1 and 2**, respectively. The solubility of Cr_2O_3 in water is so low that, as show in **Fig. 3**, it becomes possible to remove the chromium. Furthermore, Na_2O generated in the reaction in **Formula 1** also has oxidizing ability. It is possible to obtain Na_2WO_4 by the reactions in **Formulae 3 and 4**. Na_2WO_4 molten salt that is generated is rendered water-soluble, and is sent, as an aqueous solution of Na_2WO_4, to the ion exchange process. It is difficult to render vanadium insoluble in its entirety. It is necessary to remove it by ion exchange treatment.

2-4 Ion exchange process

Ion exchange treatment is performed by passing the aqueous solution through a resin tower filled with ion exchange resin, as shown in **Fig. 5**. Ion species supplied to the ion exchange resin carry out ion exchange reaction with the ion species originally captured by resin, and are adsorbed by the resin. Exchange reaction is governed by factors such as the concentrations of ion species in the aqueous solution; adsorption selectivity; and ion sizes. The purpose of the ion exchange treatment in the tungsten recycling process is to obtain an aqueous solution of $(NH_4)_2WO_4$ by so arranging that WO_4^{2-} ions contained in aqueous solution of Na_2WO_4 are adsorbed on the anion exchange resin and are eluted by an ammonium salt such as NH_4Cl (**Fig. 5**), and to remove, by molten salt solution treatment, the vanadium that was

mixed in with the aqueous solution.

As for the removal of impurities by ion exchange treatment, use is made of differences in adsorption selectivity[*1] with respect to ion exchange resin. It is known that adsorption selectivity greatly changes depending on the ion species. Tungsten and vanadium exist as WO_4^{2-} and VO_3^- under strongly basic conditions, but form "polyacids" such as $W_{12}O_{41}^{10-}$ if the pH is 7 or below. Vanadium demonstrates complicated changes due to coexistent ions in the aqueous solution. Under circumstances where WO_4^{2-} and VO_3^- co-exist with each other, heteropolyacid ions of tungsten and vanadium (W-V polyacid ions) are formed. Investigations were made of the configurations and adsorption selectivity of polyacid ions in various pH regions, with the result that it was found that there were significant differences between W-V polyacid ions and WO_4^{2-} that are generated under circumstances where the pH values of the aqueous solution are in a weakly basic region (**Fig. 6**). Under these conditions, aqueous solution containing 50 g/L of tungsten and 100 mg/L of vanadium continued to be passed through a
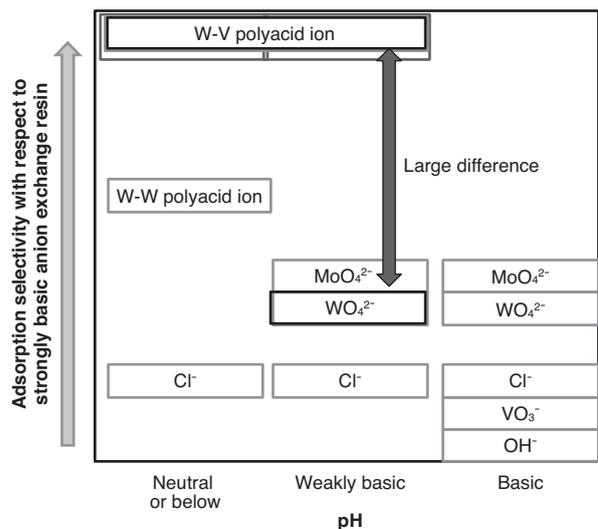
Fig. 6. Adsorption selectivity with respect to ion exchange resin

resin tower filled with ion exchange resin, and the concentrations of tungsten and vanadium contained in the liquid that leaked from the resin tower were analyzed. The analysis results are shown in **Fig. 7**. While vanadium, which has a high adsorption selectivity, is preferentially captured by the resin, tungsten, which has a low adsorption selectivity and is contained in raw material solution in a high concentration state, readily starts to leak out. After all exchange points in ion exchange resin are replaced by WO_4^{2-}, tungsten that has the same level of concentration as that of the introduced liquid continues to leak out. Therefore, a raw material solution as it will be after removal of vanadium can be obtained. After the vanadium polyacid ions arrive at the lower end of the ion exchange tower, vanadium starts to gradually leak out, thus mixing in with the raw material solution. However, as for the ion exchange resin on which the W-V polyacid ions are generally adsorbed, it is possible to decompose the W-V polyacid ions by passing a basic aqueous solution of a substance such as NaOH, with the result that the said ion exchange resin can be regenerated.
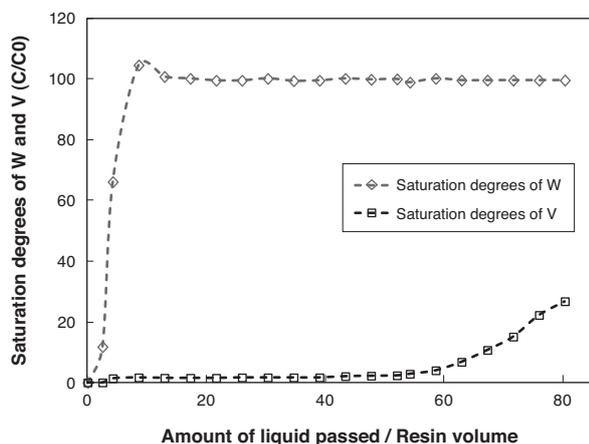
Fig. 7. Breakthrough curves for tungsten and vanadium (Saturation degree = C [Leakage concentration] / C0 [Introduction concentration] × 100)

As for the utilization of tungsten polyacid ions, not only are tungsten and vanadium separated from each other by increasing the difference in adsorption selectivity, but there is also an advantage that the treatment efficiency can be improved. The amount of tungsten that can be adsorbed per unit volume of ion exchange resin (adsorption capacity) depends on the charge number of ion species containing tungsten and on the tungsten amount. By forming tungsten polyacid ions, it is possible to adsorb approximately three times as much tungsten as the conventional amount. However, There arose a problem in that APT*2 $((NH_4)_{10}W_{12}O_{41}$, see **Formula 5**) was deposited in the ion exchange tower due to the elution treatment, resulting in the resin tower becoming clogged. It was possible to solve this problem by optimizing the elution conditions. The reaction in **Formula 5** occurs by passing NH_4Cl liquid

through the ion exchange resin on which the tungsten polyacid ions are adsorbed, with the result that deposition of APT occurs. In order to avoid this phenomenon, it is necessary to keep the aqueous solution basic, thereby decomposing tungsten polyacid ions eluted by the reaction in **Formula 6**. Consequently, $(NH_3 + NH_4Cl)$ mixed solution containing NH_3 was passed at high speed, with the result that it became possible to perform ion exchange treatment at efficiency three times as high as that in the conventional technique, without depositing APT.

$$10R\text{-}W_{12}O_{41} + 10NH_4Cl$$
$$\rightarrow 10R\text{-}10Cl + (NH_4)_{10}W_{12}O_{41} \quad \cdots\cdots\cdots\cdots\cdots\cdots (5)$$
$$W_{12}O_{41}^{10-} + 14OH^-$$
$$\rightarrow 12WO_4^{2-} + 7H_2O \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (6)$$
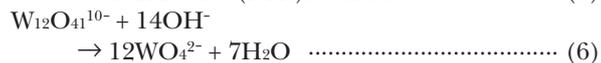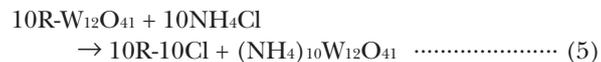
*R: This symbol signifies the exchange point for the ion exchange resin.

3. Development of Tungsten-Saving Tools by Forming Composite Structures

3-1 Development goal and concept of tungsten-saving tools

The development goal for tungsten-saving tools was set so that cutting tools in which the amount of tungsten usage is reduced by 30% would achieve equivalent performance and equivalent costs to those of conventional cemented carbide tools. Cermet, whose main raw materials are titanium (carbon, nitrogen) and which is the primary tool material second only to cemented carbide alloys, can be mentioned as a candidate material for tungsten-saving tools. Cermet has high hardness, and has low reactivity with iron. On the other hand, cermet has low toughness, low thermal conductivity, and high thermal expansion. Therefore, thermal shock resistance, R, which is represented by the following formula, is so low as to be approximately 10% of that of cemented carbide alloys.

$$R = k \cdot \sigma\kappa/\alpha E$$
where k = constant, σ = bending strength,
κ = thermal conductivity,
α = thermal expansion coefficient,
and E = Young's modulus.

As a result of the above, cermet is susceptible to thermal cracking damage due to thermal shocks caused by repeated heating and cooling. Therefore, cermet is used in limited applications such as finish processing of steel articles. As mentioned above, even in the case of cermet, which is in the closest position as an alternative material for cemented carbide alloys, there are very large performance differences with respect to cemented carbide alloys. Consequently, it was a very difficult task to develop a tungsten-saving tool material by which an equivalent performance to that of the targeted cemented alloys can be obtained and which can be manufactured at an equivalent cost. However, the authors continued studies to promptly deal with the tungsten resources issue, which was a pressing task, and aimed at solving the task by forming composite structure tools such that cemented carbide would be used in the

blade edge portions that come into contact with the workpiece, but that cermet-based tungsten-saving alloy would be used in portions not in contact with the workpiece, and by developing a manufacturing technique therefor.

3-2 Description of development of technology for forming composite structures

Figure 8 shows the flow of the processes for manufacturing a composite structure tool, and the appearance of a press-molded composite body. As for the developed processes, conventional practice is observed with regard to processes subsequent to the press-molded composite body processes, with the result that existing equipment can be utilized. The press-molded composite body is fabricated in such a way that cemented carbide alloy powder and tungsten-saving alloy powder are alternately filled into a metal mold, and subsequently, press molding is performed. This process excels in terms of cost. On the other hand, as for simultaneous sintering of the press-molded body, detachment and deformation shown in Photo 1 need to be prevented. These problems are caused by the difference of the shrinkage properties and the amount of shrinkage between the cemented carbide alloy and the tungsten-saving alloy. Another problem is that their difference in the amount of the binder phase and the interfacial energy (between the binder phase and the hard phase) causes the movement of the liquid phase generated during sintering. This movement results in the changes of the properties of the cemented carbide alloy layer which are desired to be maintained[3].

As for the restriction of detachment and deformation,
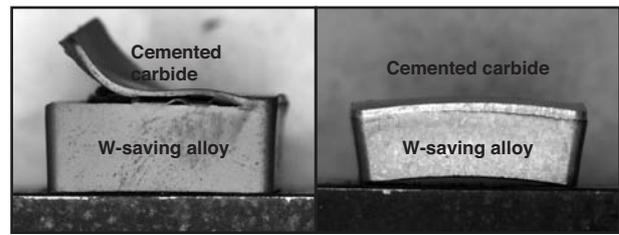
Photo 1. Appearance of delamination and deformation

it is very important to control the shrinkage properties of cemented carbide alloys and of tungsten-saving alloys. Such shrinkage properties were analyzed in detail, and development of tungsten-saving tools were pushed forward[4], [5]. As a result of this analysis, it became known that there were three large differences in shrinkage properties between cemented carbide alloys and tungsten-saving alloys. The following applies to tungsten-saving alloys as compared to cemented carbide alloys: (1) the shrinkage amount in the solid phase sintering stage at 800 to 1,200°C was smaller; (2) the timing at which shrinkage finished after densification was completed occurred later; and (3) the shrinkage rate was higher. For the purpose of improving these differences in the shrinkage properties, we investigated the relationship between shrinkage properties and factors such as pressed body densities, liquid phase appearance temperatures, and thermal expansion coefficients. As a result, by optimizing factors such as the amount of tungsten carbide added, the compositions of auxiliary agents added, and the amounts of molding auxiliary agents added, it was possible to fabricate a three-layered composite structure tool, as shown in Photo 2, which is free of detachments, and in which deformation is restricted.
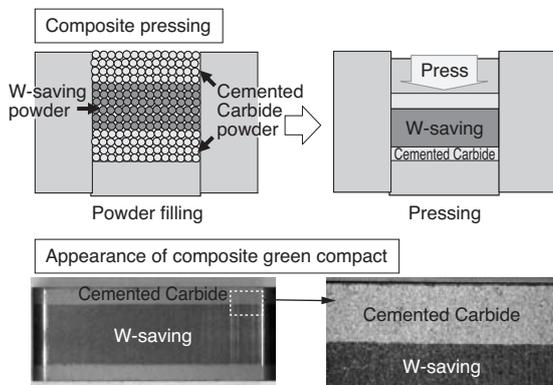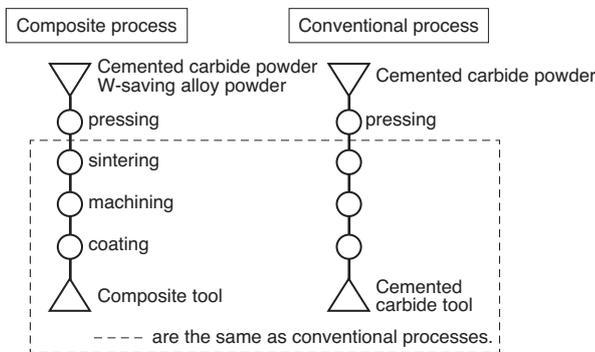
Fig. 8. Composite structure tool manufacturing processes

Photo 2. Appearance of composite structure tool

3-3 Wear resistance of composite structure tool

A PVD coating (TiAlN/AlCrN super-multi-layer coating; film thickness, 3 μm) was applied to a composite structure tool fabricated as described above, and comparative evaluation was made of cutting performance between this composite structure tool and a conventional cemented carbide tool to which the same PVD coating was applied. The results of the comparative evaluation are shown in Fig. 9. The tip shape was CNMG120408 (ISO model number). The thickness of the cemented carbide alloy in the surface layer was 1.0 mm. The workpiece was high carbon steel
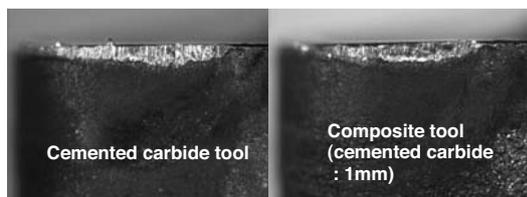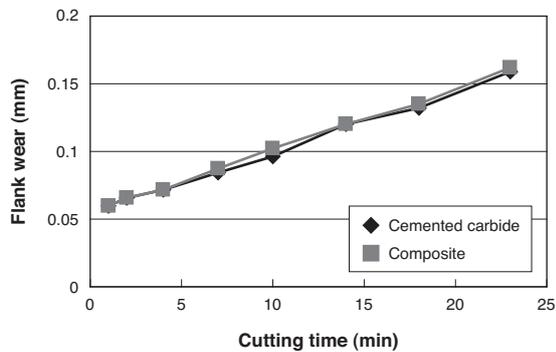
Fig. 9. Cutting performance of wear resistance

Fig. 10. CAE stress analysis results for the composite structure tool

SCM435. The cutting conditions were as follows: cutting speed, 220 m/min; feed rate, 0.3 mm/rev; depth of cut, 1.5 mm; wet type.

The flank face wear amount after the tool comprising a single cemented carbide alloy layer was made to perform cutting for 23 minutes and the flank face wear amount after the composite structure tool performed cutting for 23 minutes were both 0.16 mm, indicating that wear resistance is approximately the same. Thus, it was confirmed that a composite structure tool in which the amount of tungsten used was reduced by 30% has an equivalent wear resistance to that of a conventional cemented carbide alloy tool.

3-4 Defect resistance of the composite structure tool

In the case of tungsten-saving alloys, the amount of tungsten used is reduced in such a way that tungsten carbide used in cemented carbide alloys is replaced by titanium carbon nitride (TiCN) or the like. Consequently, thermal expansion coefficients of tungsten-saving alloys become higher than those of cemented carbide alloys. In cases where the thermal expansion coefficient of a tungsten-saving alloy, which constitutes an intermediate layer, is higher than that of a cemented carbide alloy, which forms the surface layer, compressive residual stresses are generated in the surface layer during the cooling process after densification. These compressive residual stresses can be expected to have the effect of suppressing crack propagation, thereby improving defect resistance in cutting tools. Consequently, investigations were made of the effect on cutting performance by compressive residual stresses that are generated on surface layers due to the forming of composite structures.

In order to study the magnitudes of the compressive residual stresses introduced into composite structure tools, firstly stress analysis was conducted by means of CAE[*3]. **Figure 10** shows the results of stress analysis conducted under the following conditions: the thermal expansion coefficient
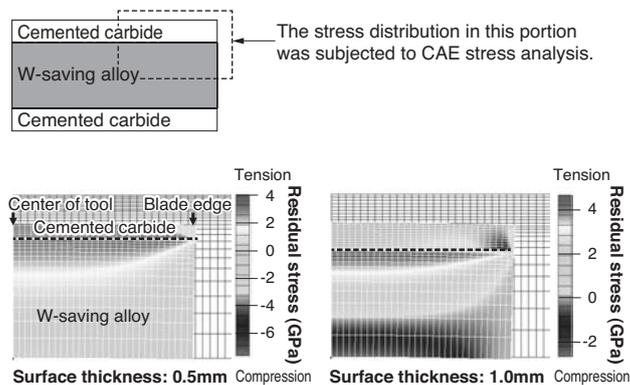
of a cemented carbide alloy in the surface layer was taken as 6×10^{-6}/K, and the thermal expansion coefficient of an intermediate layer was taken as 8×10^{-6}/K; the thickness of the cemented carbide alloy in the surface layer was changed from 0.5 mm to 1 mm. From the CAE stress analysis results, it can be seen that in the case where the thickness of the cemented carbide alloy in the surface layer is 0.5 mm, compressive residual stresses were introduced as presumed, but almost no compressive residual stress was introduced in the case of 1 mm. Furthermore, it can be confirmed that there is a tendency that the closer the blade edge portion is, the lower the compressive residual stress is.

To verify the validity of the CAE analysis results, composite structure tools having different surface layer thicknesses were fabricated, and measurements of residual stresses made. The thickness of the cemented carbide alloy in the surface layers of the composite structure tools manufactured were 0.5 mm, 1.0 mm, and 1.5 mm. As for stress measurements, Cu-Kα rays were used to evaluate WC (211) surfaces. As regards measurement locations, the vicinity of the blade edges of the cemented carbide alloy layers were measured from the side surface (flank face) side in the case
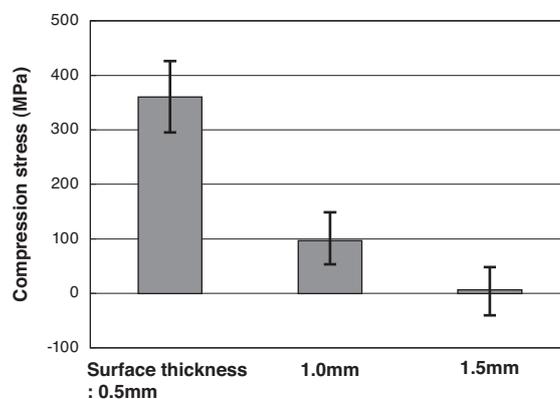
Fig. 11. Differences in residual stresses due to thicknesses of the cemented carbide alloy in the surface layer

of all specimens. The stress measurement results are shown in **Fig. 11**.

According to the results of the stress measurements, the compressive residual stress was approximately 350 MPa in the case of a surface layer thickness of 0.5 mm, and approximately 100 MPa in the case of a surface layer thickness of 1.0 mm. There was almost no residual stress as regards the surface layer thickness of 1.5 mm. Thus it was possible to confirm the tendency that the thicker the thickness of the cemented carbide alloys in the surface layer, the lower the compressive residual stress.

Furthermore, as for a specimen in which the thickness of the cemented carbide alloy in the surface layer is 1.0 mm, residual stresses was measured in the vicinity of the center of the cemented carbide apply portion in the surface layer (at locations 6.4 mm and 3.2 mm away from the blade edge). The results of these measurements are shown in **Fig. 12**. It became clear that in the vicinity of the center (1) of the specimen, compressive residual stresses tend to become higher than in the vicinity (3) of the blade edge. It was possible to confirm the tendency that the surface layer thickness and the stress distribution in the surface layer are both close to those in the analysis results based on CAE.

Next, for the purpose of investigating the influence that compressive residual stresses have on actual physical property values, measurements were made of hardness and fracture toughness[*4] with respect to composite structure tools having different thicknesses of cemented carbide alloy in surface layers. Measurements were made, starting from upper surface (rake face) portions. As for locations, measurements were made in the vicinity of positions 3.2 mm away from the blade edges in the cemented carbide apply layers. The results of the measurements of hardness and fracture toughness are shown in **Fig. 12**.
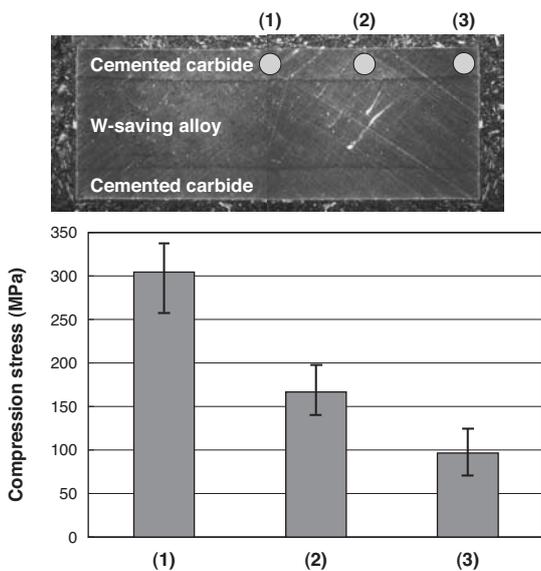
To verify the validity of the CAE analysis results, composite structure tools having different surface layer thick-

nesses were fabricated, and residual stresses were measured. The thickness of the cemented carbide alloy in the surface layers of the composite structure tools manufactured were 0.5 mm, 1.0 mm, and 1.5 mm. As for stress measurements, Cu-Kα rays were used to evaluate WC (211) surfaces. As regards measurement locations, the vicinity of the blade edges of the cemented carbide alloy layers were measured from the side surface (flank face) side in the case of all specimens. The stress measurement results are shown in **Fig. 13**.
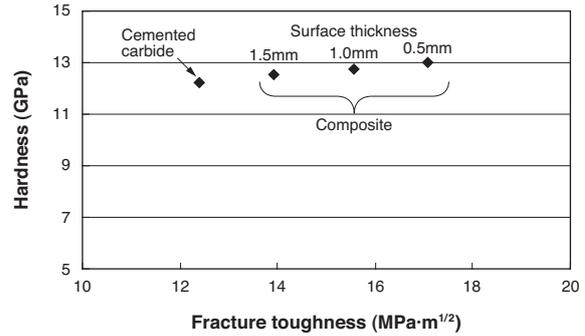
Fig. 13. Hardness and fracture toughness measurement results

It can be confirmed that in the case of composite structure tools, as compared to a tool comprising a single cemented carbide alloy layer, the smaller the thickness of cemented carbide alloy in a surface layer, the slightly higher the hardness, with the fracture toughness being the significantly higher. This is considered to be a consequence of the fact that the smaller the thickness of the surface layer, the more likely is the occurrence of the effect of compressive residual stresses generated on the interface between the cemented carbide alloy surface and the tungsten-saving alloy surface.

Figure 14 shows the results of evaluation of cutting performance of composite structure tools having different thicknesses of cemented carbide alloy in the surface layers. The tip shape was CNMG120408 (ISO model number). The thicknesses of the cemented carbide alloy in surface layers were 0.5, 1.0, and 1.5 mm. The workpiece was a channel made of high carbon steel SCM435. The cutting conditions were as follows: cutting speed, 60 m/min; feed rate, 0.5 mm/rev; depth of cut, 2 mm; dry type.

Tests were conducted at all eight corners, with the following results: A tool comprising a single tungsten-saving alloy layer is very brittle with a failure rate of 100% as compared with a failure rate of 50% in the case of a tool comprising a single cemented carbide alloy layer. As for a composite structure tool in which the thickness of cemented carbide alloy in the surface layer is 1 mm, the failure rate is 50%, which is equivalent to that of the tool comprising a single cemented carbide alloy layer. However, in the case of a composite structure tool in which the thickness of cemented carbide alloy in the surface layer is 0.5

Fig. 12. Residual stress differences due to measurement locations
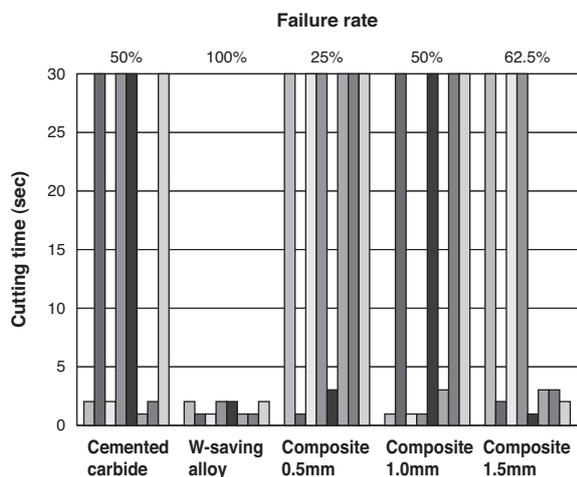
Failure rate

Fig. 14. Cutting performance of defect resistance

mm, and in which the highest compressive residual stress was produced, the failure rate is 25%. This fact demonstrates that there is an improvement in defect resistance that is approximately twice as high as that of the tool comprising a single cemented carbide alloy layer. Thus, in the case of composite structure tools, not only can the amount of tungsten used be reduced compared with conventional cemented carbide alloy tools, but also defect resistance can be expected to increase.

4. Conclusion

Efforts were made to develop a technique for recycling tungsten from cemented carbide scrap using a chemical treatment method with high general-purpose properties. It was possible to develop processes whereby tungsten can be recycled at low cost in a small-scale, yet efficient manner, in such a way that only low environmental loads are imposed. In A.L.M.T. TUNGSTEN Corp., recycling business was started in October 2011 using this technique. It is considered that some contributions can be made to the stable supply of tungsten resources by so arranging that cemented carbide tools consumed in Japan are recycled, circulated, and reused in Japan.

By developing a tungsten-saving alloy primarily composed of a cemented carbide alloy and titanium carbon nitride and formed into composite structures, success was achieved in developing tungsten-saving tools in which the amount of tungsten used was reduced by 30%. By forming composite structures, compressive residual stresses were provided to the cemented carbide alloy in surface portions constituting cutting edges, with the result that it was possible to improve defect resistance. From now on, development of a mass production technique will be promoted with the aim at practical application, and efforts will be made to create tungsten-saving cutting tools.

5. Acknowledgements

Technical Terms

*1 Adsorption selectivity: This term denotes the ease of adsorption of an ion on an ion exchange resin. The higher the selectivity is, the more firmly the ion is adsorbed on the resin, and the less liable the ion is to be eluted. Ions with high selectivity are preferentially adsorbed on the resin, and therefore readily expel ions with low selectivity from the resin.

*2 APT: Ammonium Paratungstate $(5(NH_4)_2O \cdot 12WO_3 \cdot 5H_2O)$. This substance is used as an intermediate raw material in tungsten refinement. Due to roasting, ammonia and water volatilize, resulting in WO_3 being able to be obtained.

*3 CAE (Computer Aided Engineering): This is a computer-based simulation technique.

*4 Fracture toughness: This is a numerical value that indicates susceptibility to crack propagation, and is calculated from the length of a crack generated when an indentation is formed by hitting. If fracture toughness is high, cracks do not tend to propagate, and tools are not liable to fracture.

References
(1) U.S. Geological Survey, Mineral Commodity Summaries 2007, 179 (2007)
(2) Suzuki H et al. Cemented carbides and sintered hard materials. Tokyo: Maruzen; 1986
(3) P. Fan, Z. Z. Fang & H. Y. Sohn: Acta Mater. 2007, v55, p.3111
(4) Tomoyuki Ishida, Hideki Moriguchi, Akihiko Ikegaya, "Fabrication of composite structural material of cemented carbides and cermets" Proceedings of PM2010. florence, Italy, 2010-10-10/10-14, European powder metallurgy association
(5) Tomoyuki Ishida, Hideki Moriguchi, Akihiko Ikegaya, July 2011 SEI Technical Review No.179

Contributors (The lead author is indicated by an asterisk (∗).)

T. ISHIDA∗
- Advanced Materials R&D Laboratories
  Engaged in the development of tungsten-
  saving techniques regarding CBN cutting
  tools

T. ITAKURA∗
- PhD (Engineering)
  Materials Research Department, A.L.M.T.
  Corp.
  Engaged in the development of tungsten
  recycling technology

H. MORIGUCHI
- PhD (Engineering)
  Group Leader, Advanced Materials R&D Laboratories

A. IKEGAYA
- Chief Engineer, Advanced Materials R&D Laboratories