History of Igetalloy

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Cemented carbide is a composite material of ceramics and metal, and the major structures are WC-Co and WC-TiC-Co. The advantages cemented carbide has over other materials are high degrees of hardness and wear resistance. Cemented carbide is already put into practical use in various applications, such as cutting tools, wear-resistant tools, corrosion-resistant tools and decorations, and this trend is spreading widely. Today, the annual production of cemented carbide in Japan has exceeded 6,000 tons. Sumitomo Electric Hardmetal started the research on cemented carbide 80 years ago, and has since then been working hard to develop new materials and techniques for manufacturing these. This paper provides a look back at 80 years of history of Igetalloy and also describes new materials and the latest manufacturing techniques.

1. Introduction

Cemented carbides are the ceramic-metal composites that are based mainly on WC-Co and WC-TiC-Co. The advantages cemented carbides have over other ma terials are high degrees of hardness and wear-resistance. Cemented carbides are already put into practical use in various applications such as cutting tools, wear-resistant tools, corrosion-resistant tools and decorations. Today, the annual production of cemented carbides in Japan has exceeded 6,000 tons.

The Sumitomo Electric Group started the research on cemented carbides 80 years ago, and has since then been working hard to develop new production techniques and new cemented carbide grades. This paper provides a look back at 80 years of history of the Sumitomo Electric Group's Igetalloy and also describes new grades and the latest manufacturing techniques.

2. Origins of powder metallurgy and cemented carbides

2-1 Powder metallurgy

Metal products can be made by various methods, such as powder metallurgy, casting, and forging. In 1909, W. D. Coolidge successfully invented a method to produce W wire filaments from W powder. This method, which is today called powder metallurgy, is suitable for producing cemented carbides that contain chemical elements with high melting points.

This method is suitable for high-precision or net-shape powder metallurgy, and has been evaluated as being superior to other manufacturing methods in terms of material use rate and energy consumption, as shown in **Fig. 1**.(1)

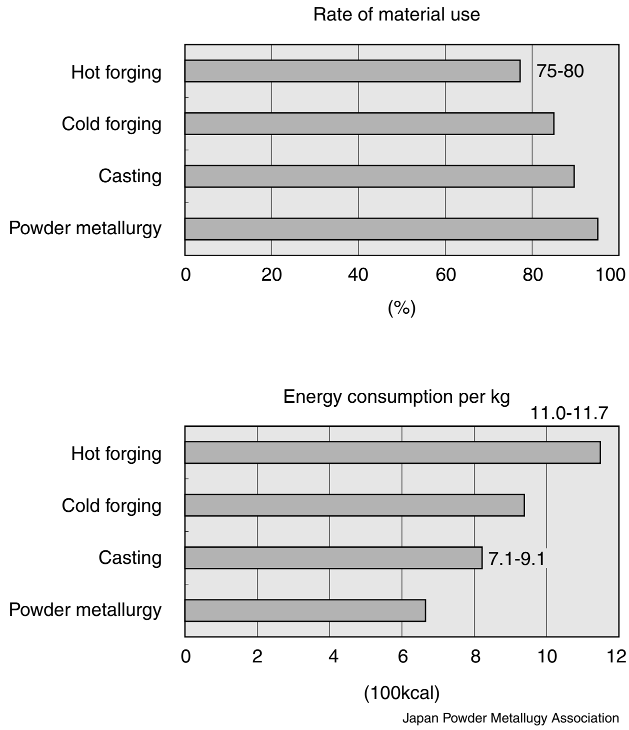


Fig. 1. Material use rate and energy consumption in different metal manufacturing methods

Cemented carbides are produced by melting binder metal Co through liquid-phase sintering. This method is performed at a temperature considerably lower than the melting point of WC (2,900 degrees Celsius).(2)

2-2 Cemented carbides

K. Schroeter of the Osram Lamp Works, a German electric bulb maker, discovered that when electric bulb filaments were drawn using special steel dies, WC appeared on die surfaces and became extremely tense. Cemented carbides originated from this finding.

After Schroeter's invention of cemented carbides by sintering WC with Co or Ni in 1923, a German company Krupp A.G. started selling cemented carbide in 1926. In 1931, R. Kieffer started marketing WC-TiC-Co-based steel cutting alloys and established a basis for the development of cemented carbides for use in cutting tools.(3)

3. Cemented carbide manufacturing at Sumitomo Electric

3-1 Early times

During 1920s, at Sumitomo Electric, as die wire drawing facilities were upgraded for faster wire drawing speed, the improvement of dies had become a pressing need. No progress, however, was observed in the development of better drawing die materials.

After obtaining information about Krupp cemented carbide in 1927, Sumitomo Electric started researching cemented carbides. Subsequently, in 1929, the Company succeeded in producing a new type of dies for in-house use by means of hot pressing (a method in which pressing and sintering takes place simultaneously). The new die was launched on to the market in 1929 under the brand name "Igeta-Hardloy." The currently registered trade name "Igetalloy" has been used since 1959.(4)

3-2 Early cemented carbide manufacturing method

In earlier days, cemented carbides were produced by the complex method. First W, C and Co powders were mixed using a ball mill, then carburized, and lastly pulverized again in a ball mill to be prepared into fine WC-Co powder. The prepared powder was hot-pressed into cemented carbide.

However, the complex method has a drawback that it is difficult to control carbon amount and WC grain size. Moreover, hot pressing has problems with mass production of small-sized items.

In 1953, Sumitomo Electric signed an agreement on technical cooperation with Metalwerk Plansee GmbH, a major Austrian cemented carbide manufacturer. As a result of this technical cooperation, the method for preparing fine WC-Co powder was replaced with the indirect method: First W and C were carburized to form WC, and then crushed and mixed with Co powder to be prepared into fine WC-Co powder. In addition, the method of alloy production was changed from hot pressing to the cold process, a method in which sintering is conducted in a batch-type furnace after pressing at room temperature. **Figure 2** illustrates the WC-Co powder preparation processes (complex method and indirect method) and **Fig. 3** describes the cemented carbide production processes (hot pressing and cold process).

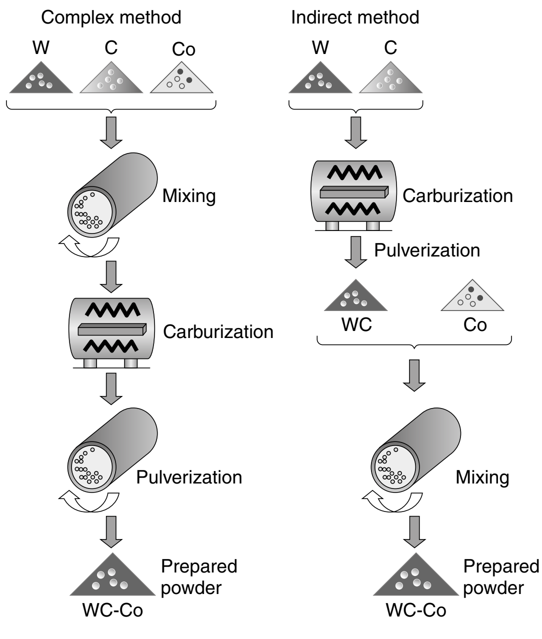


Fig. 2. WC-Co powder preparation methods (Complex method and indirect method)

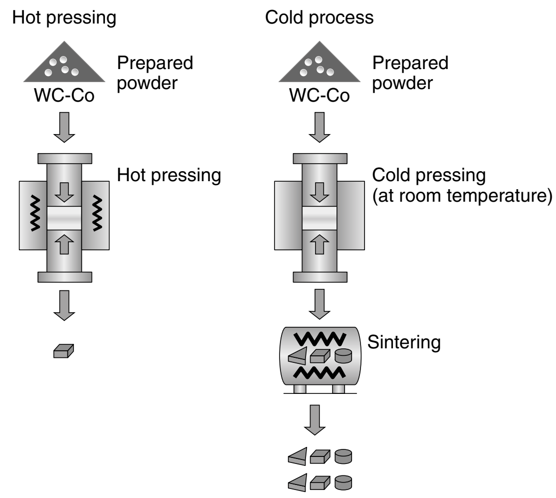


Fig. 3. Cemented carbide manufacturing methods (Hot pressing and cold process)

The technical cooperation with Metalwerk Plansee had brought enormous progresses in Sumitomo Electric's cemented carbide production technology, such as the shift of the raw material powder crushing process from dry to wet , the use of electrodeposited diamond whetstone in the molding process and the introduction of vessel vacuum sintering furnace. Remarkable progresses were observed also in the aspect of quality assurance, such as the measurement of free and combined carbon contents, saturation magnetism and Vickers hardness.

Immediately after the end of the Second World War, Sumitomo Electric supplied only few cemented carbide grades for cutting tools: Three grades including WC-Co for wear-resistant tools, three grades for steel cutting, and three grades for cast-metal cutting, all manufactured by the technology used during wartime. After the technology introduction from Metalwerk Plansee, the Company's cemented carbide grades were categorized by hardness and toughness according to WC grain size and Co content. **Table 1** lists Sumitomo Electric's cemented carbide grades for wear resistant tools in the year 1960. The basic technology of the Company's WC?Co-based cemented carbides of today was nearly completed at this period.

Also started at this period were the addition of TiC in the form of double carbide instead of single carbide and the addition of TaC and VC grain growth inhibitors to fine-grain cemented carbides.

Table 1. Cemented carbide grades for wear-resistant tools in 1960

Grades	Property tendencies		Applications
	Wear resistance	Toughness	
H2	High	Low	Tools used under small shocks (dies, nozzles, etc.)
H1			
D1			General wear-resistant tools (plugs, rolls, guide bushes, etc.)
D2			
D3	Low	High	
G5	High	Low	Shock-resistant tools (punches, dies, headers)
G6			
G7			
G8	Low	High	

4. Changes in raw material production technologies

At Sumitomo Electric, since it had started producing cemented carbides, research and study have been going on regarding the manufacturing methods of WC and Co powders and double carbides, which are the ingredients of cemented carbides.

4-1 Production of WC

In the past, Sumitomo Electric produced WC by a process described in **Fig. 4**. In the tungsten refining stage, ore is dissolved in caustic soda and washed, and then the solution is chemically refined into high-purity WO3 or its ammonium salt. The refining process had been studied with an aim of removing impurities and subsequently obtaining high-purity WO3 powder.

The reduction stage is where refined substances are reduced by hydrogen to produce W powder. During the post Second World War period, Sumitomo Electric adopted the two-step reduction approach in which WO3 is reduced to WO2 before reduced to W so as to keep reaction uniform. Single-step reduction was adopted in the 1950s after the development of rotary reduction furnace that ensures uniform reaction.

In the carburization stage, vertical high-frequency furnace had been used in the past, but it had such drawbacks as temperature inhomogeneity and unsatisfactory workability. The Company self-manufactured a continuous horizontal furnace, which had longer service life and provided higher-quality WC.

Ore
(Wolframite)

⇩

Refinement
Dissolution in caustic soda, filtration, washing
Neutralization with hydrochloric acid, dissolution in ammonium solution, filtration

⇩

Reduction (Two-step reduction)
$WO_3+H_2 \rightarrow WO_2+H_2O$
$WO_2+2H_2 \rightarrow W+2H_2O$

⇩

Carburization
$W+C \rightarrow WC$

Fig. 4. WC production process

One outstanding progress in the Sumitomo Electric's carburization technology is the practical application of the proprietary direct-carburization technology in which ultrafine WC grains are produced directly from WO3 and not from W. This technology has tremendously contributed to the Company's early development of ultrafine-grain cemented carbides.[5]

In expectation of future production expansion and new technology development, it was determined the refining and carburization operations were consolidated at A.L.M.T. Tungsten Corp. and all works related to operation transfer were completed by the 1980s.

4-2 Production of Co

Before and during the Second World War, Co powder used to be produced through either hydrogen reduction of Co oxide imported from overseas or direct electrolysis of Co shots. These methods had a drawback in term of grain size. After the war, the Company began self production of Co oxide through a process in which Co is dissolved in nitric acid, filtered to remove impurities, dried and roasted. Because this process had the problem with achieving high purity Co powder, the hydroxide method was introduced to refine Co nitrate solution. The obtained Co oxide was reduced by hydrogen to be formed into Co powder.

In the late 1960s, it had become possible to import high-quality Co powder from overseas at reasonable price, and eventually the Company ended self-production.

5. Cemented carbide manufacturing process

5-1 Molding

In the cold process used at Sumitomo Electric to manufacture cemented carbides during and after the Second World War, WC-Co composite powder prepared by the complex method was compression molded into small blocks using a hard press, went through the pre-sintering step, and then pre-treated using a hand file or hacksaw. Because no binder component was included in the composite powder of the time, the powder was coarse and slippery. The press itself provided inhomogeneous pressure and work efficiency was very poor.

After technology introduction from Metalwerk Plansee, camphor and ether were added as binders to the composite powder prepared by the indirect method, and a variable-pressure hydraulic press was used. Pressed blocks were pre-sintered at an optimal temperature depending on material types and grinded with high dimensional accuracy using an electrodeposited diamond wheel.

In order to prevent the oxidation of pressed bodies and powders that causes the deterioration of product quality, the press chamber and the powder storage room have been air conditioned since then. In addition, waste powder generated during the shape-forming process has been recovered according to grade and reused in the preparation of the composite powder. This has contributed to the improvement of the rate of powder use and resulted in the marked decline in material loss.

The past-used method of separate pressing (pressing one object at a time) was inefficient because the composite powder lacks fluidity and weight measurement must be done every time before the powder is poured into a metal die. In order for the composite powder to be poured into metal dies continuously, the powder needed to be granulated into a uniform grain size. This approach was made possible after the practical introduction of spray dryer in the 1970s.

The other molding method put into practical use was cold isostatic pressing (CIP), which was applied to the production of items in the form of round bars and in large sizes. In the CIP process, powder is put into a rubber mold and pressured through a pressurizing rubber mold under isotropic pressure and using fluid as a pressure media.[6]

Moreover, the extrusion process was practically applied for manufacturing products that are long in length and have uniform cross-sectional shape, such as round bars. In the extrusion process, the material is required to have appropriate levels of plasticity, lubricity and mechanical strength, and therefore a larger amount of binder needs to be added to powder as compared with other processes.[7] The drawback of the extrusion process is that because more amount of binder is required, it is difficult to debinder. This eventually leads to the problem of pores remaining in sintered bodies. This drawback puts limitations on extrusion diameter and therefore the maximum diameter of sintered alloy products is also limited. Recently, as binder materials advanced, it became possible to produce round bars with diameters as large as 25 mm.

5-2 Sintering

In the post Second World War period, Sumitomo Electric performed sintering in hydrogen atmosphere using a horizontal Mo furnace. Later the Company used carbon instead of the heater and used a high-frequency furnace for vacuum sintering. The problems encountered in those days were surface decarburization during low-vacuum sintering and volatilization of Co during high-vacuum sintering. In the latter half of the 1970s, the Company introduced the atmosphere sintering technique that allows carbon contents in alloys to be finely controlled, and succeeded in reducing product deformation (warpage).

After 1990, tight box has been installed between the heater and the object to be processed. **Figure 5** shows the schematic view of tight box structures. In the de-wax process, carrier gas is drawn from outside the tight box and the inside is vacuumed so as to differ pressure between the inside and outside of the tight box and prevent wax from flowing beyond the tight box, thus eventually preventing the furnace from being polluted by wax. Tight box acts as a full-face heater that generates second radiation to the object to be processed and contributes to the improvement of temperature distribution during the rise and holding of temperatures. [8]

Recently, cascade temperature control by which the temperature around the objectto be processed is monitored and controlled has been developed. Using the tight box structure prevents wax from adhering to the furnace, which is advantageous for maintaining a clean condition even during compulsory gas cooling. The method mainly used at present is to shorten cooling times and sintering process cycles by applying pressure (0.3 to 0.8 MPa) to the cooling gas.

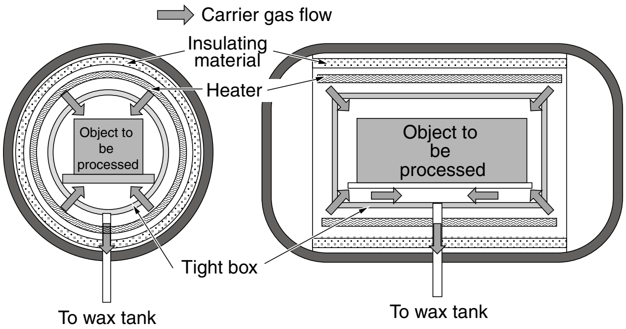
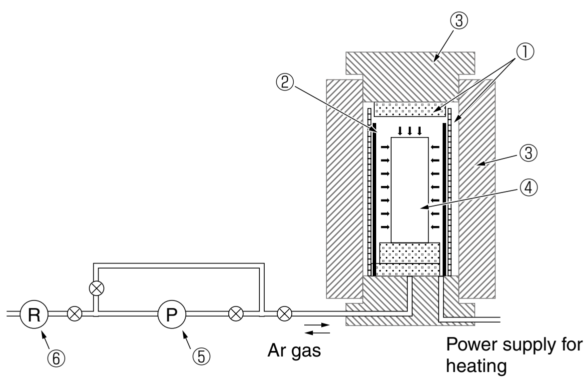


Fig. 5. Tight box structures

5-3 Hot isostatic pressing (HIP)

Cemented carbides are sintered by liquid-phase sintering, which, however, leaves residual pores in sintered bodies. These pores shorten tool life and may be identified as critical defects in some products. Earlier in the 1970s, hot isostatic pressing (HIP) was established by many cemented carbide makers around the world.

Figure 6 schematically illustrates the process of HIP, which is performed in high pressure Ar gas around 100 MPa at a high temperature around one thousand and several hundred degrees. [9] Also presently being put to practical use is Sinter-HIP, which is performed in low pressure around 10 MPa following the sintering process. It has been confirmed that for some grades, HIP at low pressure around 10 MPa provides an equal performance as that at around 100MPa. As indicated in **Fig. 7**, HIP removes pores and significantly improves transverse rapture strength (TRS), resulting in conspicuous enhance-



①Insulation material ②Heater
③Container ④Object to be processed
⑤High-pressure gas compressor
⑥Ar gas tank

Fig. 6. Schematic view of HIP system

ment of product reliability. TRS improvement by HIP is more effective with grades containing less amount of Co, Treatment by HIP is essential for alloys such as those for PCB drills (drills for drilling printed circuit boards).[10]

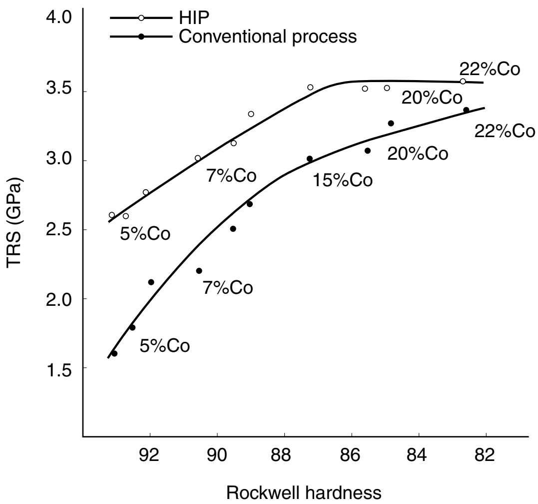


Fig. 7. TRS improvement by HIP

6. Cemented carbide quality enhancement

6-1 Coatings and cemented carbide grades suitable for cutting tools

Among various new cemented carbide grades for cutting tools developed since the 1950s, A40 was an epoch-making cemented carbide that had become a major grade for tools for cutting high-speed tool steels. A tough cemented carbide developed in the 1970s was A30, which realized excellent thermal crack resistance by adding nitrogen. A30 became the most popular grade for milling tools, and was also used for drills for steels. A tougher nitrogen-added cemented carbide was developed as A30N, which had become the best selling grade for milling tools.

Earlier in the 1970s, a European manufacturer commercialized coated cemented carbides. Cemented carbides coated with ceramics such as titanium carbide (TiC), titanium carbon nitride (TiCN) and alumina (Al2O3) substantially improve cutting tool properties (wear resistance, oxidation resistance and adhesion resistance). Coating methods that are practically used are chemical vapor deposition (CVD) and physical vapor deposition (PVD). Because of its high coherence strength, the CVD method is applied for manufacturing cutting tools and other tools that require wear resistance.

The PVD method was put into practical use for the first time by Sumitomo Electric. The method has an advantage that the deterioration of base material strength is almost zero. As cutting conditions become more severe, more coated indexable inserts were launched to the market and coatings were required to have a multilayer structure. The technology of coating is presently gathering much attention and its improvement is accelerating.

6-2 Cermets

Cermets used as machining tool materials are composed mainly of titanium compounds (TiC, TiN and TiCN), which are highly resistant against oxidation and adhesion and provide smooth finished surface. Cermets having additional amounts of nitrogen can have high levels of durability and heat resistance equal to those of cemented carbides. Recently, this type of cermets is receiving a lot of attention from the aspect of W saving.

6-3 Grades suitable for wear-resistant tools

Alloys developed for the purpose of manufacturing wear-resistant tools include the M series grades with higher amounts of Ni and Cr that show outstanding resistance against corrosion and oxidation, and also the BL series grades containing almost no residual binder that have high wear resistance several tens of times that of conventional cemented carbides. The M series grades are suitable for making equipments used at chemical plants where both corrosion resistance and wear resistance are required as well as for wear resistant tools that are used with corrosion resistant lubricants.[11] The BL grades are suitable for making equipments such as water jet nozzles and blast nozzles that are used in applications where shock is small but abrasive wear occurs due to constant rubbing motions.[12]

6-4 Superfine grain alloys

Sumitomo Electric produces superfine grain WC using its proprietary direct carburizing method and has been a leader in the manufacture of superfine grain alloys. Superfine grain alloys can be defined as alloys that contain WC particles 0.7 μm or smaller in diameter.

The most popular product made from superfine grain alloys is PCB drill. As demand for smaller-diameter PCB drills grows year by year along with the increasing production of highly integrated circuit boards, requirements for grades for drills are becoming stricter. To meet the strict requirements of PCB drill users, Sumitomo Electric developed the highest-quality superfine grain alloy ZF20A.

The Company had combined its knowledge and experience and made concerted efforts to clarify and set up production procedures and conditions so as to optimize alloy compositions, select quality raw material powders, improve powder crushing method, improve WC-Co powder quality and select proper press dies for smoother transmission of press pressure, and determine the optimum heating and cooling conditions in the sintering step. **Photo 1** shows the homogeneous and defect-free

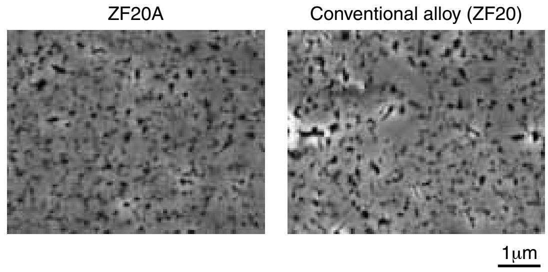


Photo 1. Microscopic structures of ZF20A and ZF20

structure of ZF20A, and **Fig. 8** shows ZF20A's transverse rapture strength (TRS). **Figure 8** suggests that the minimum value of TRS for ZF20A is significantly higher compared to ZF20, which has resulted in the improvement in the reliability of drills.

The quality of ZF20A is guaranteed by the specifications stricter than those for conventional alloys and also by the Company's efforts to ship only best quality products to customers realized through activities such as high-magnification observation of alloy structure and inspection of structural uniformity.

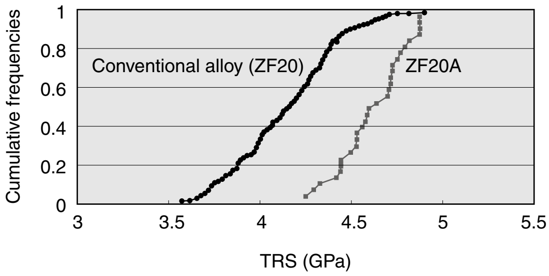


Fig. 8. TRS of ZF20A and ZF20

7. Raw material recycling

7-1 Current problems

The main components of cemented carbides, such as W, Co, Ni, Cr and V, are rare metals. These rare metals are produced in an extremely limited number of countries such as those listed in **Table 2**. The global consumption of rare metals is increasing due to the economic growth of countries like China and India. Japan has been a large consumer of rare metals; it is the largest consumer of Co and the fourth largest consumer of W.[13] Since the Japanese industries dependent largely on the import of rare metals, their survival is greatly influenced by the moves in producing countries. Meanwhile, China who produces 80% of the global W supply is promoting a national policy on further protection of its natural resources. China is implementing a policy of imposing export tax and export license on W since 2006, provoking a great deal of anxiety for future supply of W. The price of ten tons of APT, an intermediate W product, was sixty-six US dollars in 2003, but jumped to two hundred and sixty US dollars the following year. In response to rising W prices, Sumitomo Electric is presently collaborating with other member companies of the Sumitomo Electric Group in diversifying raw material supply sources.

7-2 Recycling

Recycling of rare metals is vital in view of global supply trend. Because W is an expensive rare metal, many cemented carbide makers have been recycling W since a long time ago. At Sumitomo Electric, cemented carbide scraps are being recycled since the 1940s through oxidizing roasting at about 1,000 degrees Celsius in the open atmosphere followed by refinement processes. The high-temperature process, zinc process and cold stream process were developed as low-cost W recycling processes. Sumitomo Electric had paid particular attention to the zinc process and put it to practical use in the latter half of the 1970s.

In the zinc process in which the treatment is performed at below 1,000 degrees Celsius, no WC grain growth takes place and therefore recycled W powder has the same composition as the original scraps. Sumitomo Electric had improved the sorting and recovery technologies, the process for preventing impurity incorporation and furnaces, and developed a new grade that uses W powder recycled by the zinc process. In 1996, W powder recycled by Sumitomo Electric's zinc process were evaluated by the technical committee of the Japan Cemented Carbide Tool Manufacturers' Association, and the Association's member cemented carbide makers rated it appropriate for practical use. Since 2007, Sumitomo Electric resumed the W refinement process and is promoting further enhancement of the zinc process since then.

8. Conclusion

Cemented carbides that feature outstanding toughness and wear resistance have contributed greatly to the improvement of the precision of machinery parts as well as to the reduction of manufacturing costs. Sumitomo Electric is committed to further improving production technologies and developing new grades so as to strengthen its market competitiveness and enhance user satisfaction.

※Igetalloy is a trademark of Sumitomo Electric Hardmetal Corporation.

Table 2. Top 3 producers of rare metal for cemented carbides by market share

	#1		#2		#3		Total share of top 3 producing countries
Tungsten	China	90%	Russia	4%	Austria	2%	96%
Cobalt	Congo	31%	Zambia	17%	Australia	13%	60%
Nickel	Russia	22%	Canada	15%	Australia	14%	51%
Chrome	South Africa	43%	India	19%	Kazakhstan	19%	81%
Vanadium	South Africa	42%	China	34%	Russia	21%	98%

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