New material development by the integration of cast technology and powder metallurgy technology

— A high-performance hard material which used intermetallic compound for binder phase —

Keizo Kobayashi*, Kimihiro Ozaki, Akihiro Matsumoto and Hiroyuki Nakayama

[Translation from *Synthesiology*, Vol.3, No.4, p.301-308 (2010)]

Hard materials made of ceramics combined with metals are used for dies and cutting tools that support high precision processing technology in Japan. Hard materials, however, need a large amount of rare metals that are scarce as resources as component and hence developing new materials with less dependence on rare metals has been expected. We developed a new hard material with Fe-Al intermetallic compound as a binder. This material was synthesized by a process combining casting and powder metallurgy and exhibited high hardness and high strength simultaneously. This paper introduces an approach to "*Type2 Basic Research*" in order to apply the developed material to industrial use, and a method of efficient research and development through the collaboration of researchers of different specialized fields.

Keywords : Cemented carbide, FeAl, mechanical alloying, pulsed current sintering, die, cutting tool

1 Background of research

Cemented carbide, which is widely used in molds and cutting tools, is a composite material with high strength and hardness. It is fabricated by sintering hard tungsten carbide with cobalt. It is an essential material for precision machining technologies, which are used by many Japanese advanced industries, for example, automobile industry and information appliance industry. Cemented carbides have a long history. Japanese exports of carbide tools are increasing annually, with an increase of over 350 billion yen reported in 2007 (statistics according to the Japan Cemented Carbide Tool Manufacturers' Association). However, with increasing global industrialization, concern over the long-term stable supply of tungsten and cobalt is growing. Particularly, the rare metal cobalt has been subject to radical price fluctuation. Furthermore, the development of a new metallic binder phase is highly desirable from the environmental perspective. For these reasons, AIST started directing efforts toward the development of a new composite material of a metal and ceramic with high strength and hardness.

An ideal metal for use in these composites is iron, which is an abundant resource with a stable price. However, the use of iron presents significant challenges owing to its high reactivity with carbides (e.g., tungsten carbide) and its propensity to rust. Therefore, cemented carbides with iron as the binder phase have not been previously used practically. However, there is a demand for cemented carbide for use in high-temperature applications in the machining industry. For example, the use of cemented carbide in cutting tools will facilitate both high-speed cutting and unlubricated cutting, and its use in molds will facilitate forming processes in middle to high temperature ranges. It is anticipated that such applications will reduce energy consumption during the forming process, contributing to the goal of achieving a low carbon society. It is essential to provide heat resistance to the binder phase of the cemented carbide for these applications.

In this paper, we describe the development at AIST of a new cemented carbide using an iron aluminide intermetallic compound[1] as the binder phase. We present an evaluation of its mechanical characteristics and a property evaluation required for its industrial use and applicability to peripheral technologies. This research was carried out by a group consisting of several researchers with different specialties.

2 Objectives and goals of the research

The effective use of intermetallic compounds to improve the heat resistance of hard composites is well documented, with reports of comprehensive studies by universities, private companies, and national institutes in the project of the Ministry of Economics, Trade and Industry since 1990. As a consequence, intermetallic iron-based materials were considered. Intermetallic compounds comprise an ordered phase of different metal elements, and are known to exhibit properties somewhere between those of ceramics and metals. Particularly, the aluminum-based intermetallic compound called "aluminide" shows reverse temperature dependency of the material strength, and offered promise as a metal-based material for use in the middle-high temperature range. Through collaboration with private companies, AIST has previously studied the synthesis of aluminide

Materials Research Institute for Sustainable Development, AIST 2266-98 Anagahora, Shimo-Shidami, Moriyama-ku, Nagoya 463-8560, Japan * E-mail : kobayashi-keizo@aist.go.jp

Original manuscript received July 30, 2010, Revisions received August 25, 2010, Accepted August 30, 2010

intermetallic compounds using casting technology, synthesizing intermetallic compounds including titanium aluminides (TiAl, Ti_3Al, etc.) and iron aluminides (FeAl, Fe_3Al, etc.). Because the aluminide intermetallic compounds are composed of elements with large specific gravities and large melting point differences, the degree of segregation proved too large for the traditional melting method or casting technique. Therefore, a new process technology called levitation melting and casting was developed. However, through simply casting the molten metal, the microstructure of the iron aluminide intermetallic compound became coarse, and sufficient strength could not be obtained. At the same time, AIST was developing the semi-solid forming technology as a casting technique for shaping magnesium alloy with fine microstructure. This technique involves the application of high pressure to partially molten alloy, and produces both the near net shaping by thixotropic properties and the high strength given by fine microstructure. Moreover, we considered powder metallurgy technology as a synthetic method for the production of aluminide intermetallic compounds, and investigated the synthesis of aluminide intermetallic compounds with fine microstructure using the mechanical alloying method[2]-[4].

With the technologies for the material design and manufacturing processes almost completed for the WC-Co cemented carbides, the research was conducted mainly for the development of finer hard particles. The demand for cemented carbides has increased with the increased speed and precision of machining technology, and as a consequence, there have been further demands for cost reduction. Particularly, an alternative to, or means of reducing the amount of, cobalt (which can be subject to extreme price fluctuation) and tungsten (which suffers from variable resource availability) was sought.

Therefore, we started the development of a new process technology for a new hard material using an aluminide intermetallic compound as the binder phase by fusing technologies, i.e. the various known technologies for intermetallic compound synthesis and technologies based on our knowledge of cemented carbides. By using Fe and Al instead of Co as the binder phase of cemented carbides, we developed a process in which only Al was liquefied in the sintering process, followed by the synthesis of a FeAl intermetallic compound. By using this technology, we created a new hard material with heat resistance, as a result of compositing the hard particles of tungsten carbide, titanium carbide, or titanium boride using this iron aluminide intermetallic compound as the binder phase. To enhance the feasibility of this new material replacing conventional WC-Co cemented carbides, we set the goal for the newly developed composite material to exhibit 900 Hv or more in hardness and to surpass 2 GPa in three-point bending strength.

3 Research scenarios to realize our goals

In this technological development, the mechanical strength of the composite material was determined by the close contact force of hard particles and iron-aluminide intermetallic compounds, which filled the gaps between these particles. The method of fabricating a porous preform of hard particles and then pressure-injecting the molten iron aluminide intermetallic compound, and the method of mixing and stirring the hard particle powder into the molten iron aluminide intermetallic compound were investigated, but sufficient strength could not be obtained owing to low adherence between hard particles and intermetallic compound in this method. Therefore, we studied a new process in which hard particles of high melting point are forcibly mixed by mechanical stirring[4] with the iron and aluminum powders that are the components of the intermetallic compound as the binder phase. We believe that the hard particles were coated with metallic powders, since the metallic powder is highly ductile.

Following this, we fabricated a WC-FeAl alloy (WC-8.6 mass% Fe-1.4 mass% Al) using a method that was similar to a manufacturing process for conventional cemented carbides. WC powder, Fe powder and Al powder were wet-mixed by attrition ball milling at desired constituent and sintered at 1440 ºC in a vacuum. The conventional cemented carbide (WC-Co) was fabricated by liquid-phase sintering in which the binder phase was melted; high-temperature sintering was also necessary in the case of WC-FeAl to increase the adherence of the binder phase and hard particles. The obtained sintered compact showed excellent resistance to oxidation, even when heated to 800 ºC in air, and when the compact was treated by hot isostatic pressing (HIP), the bending strength was maximum 1.8 GPa. However, strength variations were observed in the obtained compacts, and it proved difficult to manufacture a stable compact; the composition and volume of the binder phase could not be accurately controlled as Al with a low melting point evaporated during vacuum sintering. In addition, the evaporated Al may adhere to the graphite electrode and other devices in the vacuum sintering furnace, and the fabrication of this WC-FeAl hard material using the conventional process was considered impractical.

The evaporation of Al during sintering may be caused by the insufficient reaction of Fe and Al during wet mixing. To address this, we then applied the mechanical alloying (MA) method, which is a dry mixing method that uses large mixing forces to synthesize the alloy, to produce WC-FeAl. It has already been established that the MA method for aluminide intermetallic compounds can be achieved using an amorphous alloy powder and that a significant time is needed for the alloying of Fe- and Al to progress. When the long-term MA was conducted at high energy, the adherence of the hard particles and the binder phase strengthened, and sintering at low temperature could be expected. The long-term MA was carried out using planetary ball milling, and the obtained mixture was then sintered at 1200 ºC[5] to produce a material with a fine microstructure. However, the bending strength of the compact was only 0.8 GPa. No improvement in strength was observed with increased quantities of binder phase, with the binder phase flattening out progressively[6]. Thus, even by expanding the conventional cemented carbide manufacturing process, we were unable to achieve a WC-FeAl hard material with the desired properties. Consequently, we entered the so-called "valley of death"; however, we were unable to continue the joint research with the companies, and the road to realization seemed to be closed.

Therefore, we abandoned the conventional WC-Co cemented carbide manufacturing process, and shifted to the application of pulsed current sintering technology, which our research group developed as a method for bulk compacting amorphous powders, for sintering our WC-FeAl hard material. Pulsed current sintering is a technology for fabricating a sintered compact with a fine microstructure in a short time and at low temperature by electrically heating and pressing simultaneously. It is a suitable technique for solid phase sintering. Since the pressing separated the liquid, this method was considered unsuitable for the sintering of cemented carbides that feature a liquid phase. However, a desired intermetallic compound was synthesized through the reaction of Fe and Al before the Fe was melted in the sintering process, when the homogeneous mixture of WC and Fe produced in MA was sintered after adding Al powder. Using this reaction, the Al melted at low temperature (660 ºC) in the pulsed current sintering, and the sintering progressed as the FeAl intermetallic compound was formed. Since the Al content in the WC-FeAl hard material was small, the Al liquid only infiltrated the gaps in the powder and did not separate by the pressing. By using the pulsed current sintering, the interior of the sintered compact could be heated evenly by Joule heating between the powders. In general powder metallurgy processes, organic lubricants are used during pressing and forming, but in this new process, the molten Al was thought to play the role of the lubricant. The pressing and forming in the presence of molten Al employed the same mechanism as the semi-solid forming technology, and we succeeded in obtaining the densified compact by utilizing our knowledge from the semi-solid forming technology of the Mg alloy. The reaction between Fe and Al was slightly heat generating, and a slight volume change occurred during the synthesis of the intermetallic compound to produce pores, but WC-FeAl compact could be sufficiently densified by subsequent heating. The developed process is shown in Fig. 1. The obtained WC-FeAl compact almost met our desired bending strength and hardness prerequisites[7][8]. We were finally able to make an object as a new hard material. In the new fabrication process, which combined the dry powder synthesis process and the pulsed current sintering process[9]-[11], we were able to fabricate a prototype of a new hard material that might replace some of the conventional cemented carbides, though still at laboratory level. However, the Al addition was considered to be a taboo in the conventional cemented carbide and was not accepted readily in the associated industry. Additionally, as it required special sintering equipment, the research and development for the practical use could not progress, despite the fundamental technology being in place.

Analyzing the process of fundamental technology development, the improvement of material properties were enhanced not only by our basic knowledge of cemented carbide but also the various approaches of numerous researchers with diverse knowledge of powder metallurgy, pressure sintering, and the technology to observe the microscopic region of controlled boundaries, who became interested in this hard material, for which AIST owned the composition patent. As a result, we were freed from the bind of the conventional cemented carbide manufacturing process, and were able to develop a new process based on novel ideas. Since the researchers engaged in solving this problem each had their own individual approaches, unique technologies that reflected the individuality of the researchers were

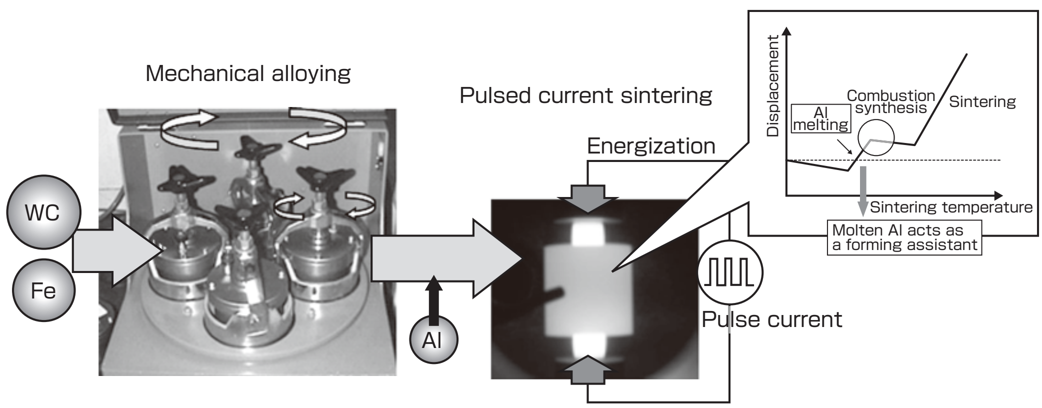

Fig. 1 Preparation process of newly developed WC-FeAl hard material

developed in the stage from *Type 2 Basic Research* to product realization.

4 From *Type 2 Basic Research* to product realization

For the newly developed WC-FeAl hard material to be adopted widely as a practical material, it was important to find companies that would manufacture this material on an industrial scale. Even if the new material could be manufactured with the new process and showed excellent properties, no company that wished to engage seriously in this material could be found. However, as we have been presenting our information about the new hard material at academic conferences (the Japan Society of Powder and Powder Metallurgy) and elsewhere, industries were interested from the initial stages of the research. Therefore, to promote the practical use of the new material, we decided to collect experimental data deemed necessary by the companies by suggesting the products for which the material could be used. We positioned this stage as the *Type 2 Basic Research* that was difficult to carry out at universities or companies owing to the high-risks involved. We utilized the AIST “High-Tech Manufacturing” project and carefully scanned the keywords for using the WC-FeAl as a mold. The technological topics for realization were: (1) fabrication of large sintered compact for a practical mold, (2) a finishing process by conventional machining technology to determine the machining cost of the WC-FeAl hard material, and (3) resistance to thermal shock by heating-cooling, assuming the use of the mold in high temperature. Since some of the problems could not be addressed in our laboratory setting, we sought cooperation from universities and companies.

In the fabrication of the large sintered body, as the pressure forming using the molten Al was used in the developed process, we found that molten Al functioned as the forming additive and the densification of the sintered body could be achieved with relative ease. By using high-voltage sintering equipment of greater capacity and applied pressure than that available at AIST, a large sintered compact with the same function as that achieved in the basic research was fabricated. The obtained large sintered compact is shown in Fig. 2. Its size (φ140 mm) would allow its use as a small mold. In the finish of the cemented carbide product, electro arc machining and wire cutting were used. These processes took advantage of the high conductivity of cemented carbide. Since the developed WC-FeAl sintered compact had high conductivity similar to conventional cemented carbides, wire cutting and electro arc machining could be used under the same machining conditions. In the wire cutting process of conventional cemented carbide, the machined surface reacted slightly and became discolored. However, there was little reaction in the case of WC-FeAl hard material owing to the good acid resistance properties of the FeAl phase. The WC-FeAl hard material sintered at AIST was processed into a mold (for small gear manufacture) at a machining company, and the appearance of the finish was the same as that obtained with a cemented carbide mold, as shown in Fig. 3. The time required for machining was about the same as the conventional cemented carbide. It was also confirmed that the new hard material could be processed at similar cost to the conventional cemented carbide. If this mold could be used for high-temperature forging, the processed material could be heated and then formed at high speed with a small forming load at high temperature, and the energy required for the process could be reduced. In general high-temperature forging, the molds are sometimes water-cooled. Therefore, we performed an experiment in which cemented carbide was heated to 900 ºC in air and then quenched in water. The appearance of the rapidly cooled samples is shown in Fig. 4. In the conventional cemented carbide, oxidation progressed rapidly, an oxide layer formed on the surface of the sample heated in the air producing a blue color, and cracks were produced due to heat stress when cooled rapidly. On the other hand, while the WC-FeAl hard material became slightly reddish-brown due to the thin oxide layer on the surface, it did not produce cracks. The developed WC-FeAl hard material did not readily oxidize when heated in the air, produced few cracks when water-

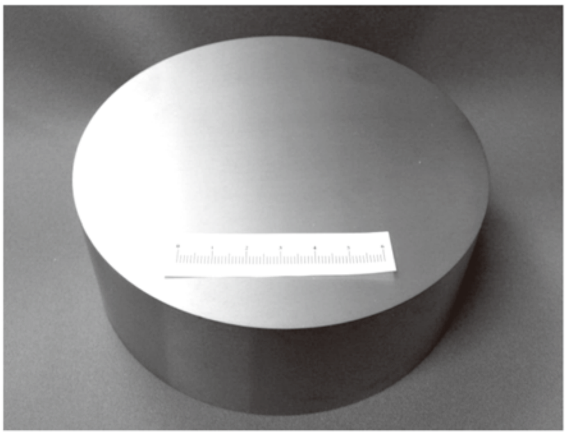

Fig. 2 Photograph of a large-size WC-FeAl sintered body

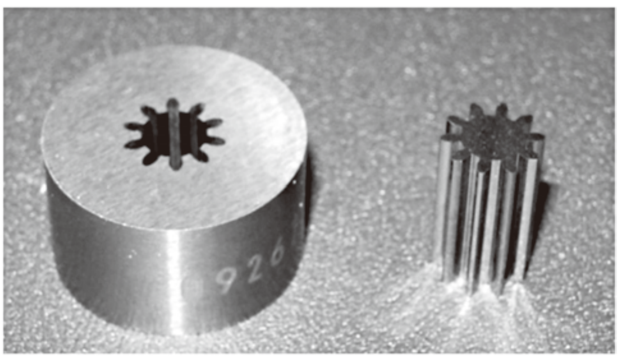

Fig. 3 Photograph of the mold made using WC-FeAl

cooled, and could be envisioned for use as mold material for high temperature.

Moreover, the WC-FeAl hard material showed machining precision at processing speeds equivalent to the conventional cemented carbide in the grinding process using abrasive stone. A prototype of the complexly shaped blade of a ball end mill was fabricated. This blade tip was able to perform equally to conventional cemented carbide, as shown in Fig. 5. However, in this ball end mill, the new material was used only at the tip that was joined to the high-speed steel rod by brazing. This was because a long sintered compact cannot currently be fabricated with the newly developed process, this being a subject for future study.

The result of this *Type 2 Basic Research* greatly reduced the timescale to the adoption for practical use. Several companies expressed desire to actually use this material. All of these companies wished to manufacture the material on their own. They wanted to introduce the new process technology, and then investigate the practical uses and business applications by combining the new technology with their own technology. Therefore, we set the cutting tools and molds as the outlet, and performed the examination to practical use through the research involving the material manufacturers and the machining companies.

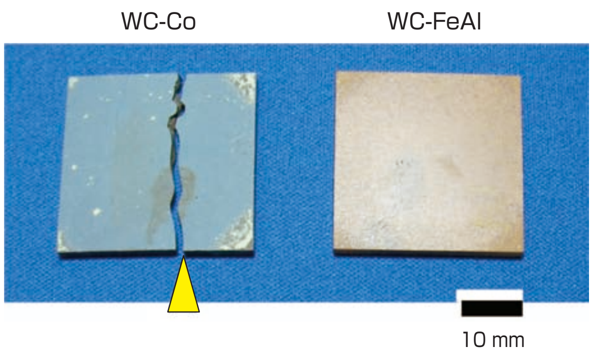

Fig. 4 Photograph of WC-based hard materials quenched in water from 900 °C in the air
WC-Co (conventional material) is cracked, but the WC-FeAl is not cracked.

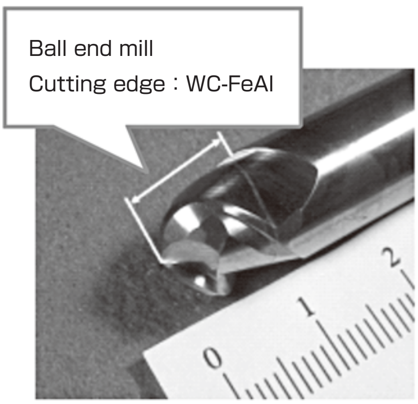

Fig. 5 Prototype ball end mill made using WC-FeAl

5 Discussions

The developed WC-FeAl hard material is a new composite material using FeAl intermetallic compound as the binder phase, and has the potential to resolve the problems associated with conventional WC-Co cemented carbide. For example, Co, which is the binder phase of the conventional cemented carbide, has a Vickers' hardness of 130 Hv, and is softer than tungsten carbide. Therefore, when the surface of the cemented carbide is polished, some unevenness occurs between the binder phase and hard particles. On the other hand, the FeAl intermetallic compound has a Vickers' hardness of 320 Hv, and the unevenness caused by the hardness difference between the binder phase and hard particles should be reduced. To examine this, the WC-FeAl hard material in which the volume ratio of the binder phase had been adjusted, and the conventional WC-Co cemented carbide were both polished with diamond abrasives, and the surfaces were coated with diamond-like carbon (DLC) by sputtering. Although there were some differences due to the observed area in the coarseness of the polished sample surfaces, values were Ra = 4.3 nm for the WC-FeAl, and Ra = 5.3 nm for the WC-Co; the polished surface was smoother in WC-FeAl because the binder phase was hard. When the adherences of the DLC film formed on each hard substrate were measured by a scratch test, the WC-FeAl required approximately 25 % higher load for separation. It was confirmed that in the boundary between the DLC film and the cemented carbide substrate, the even DLC film adhered

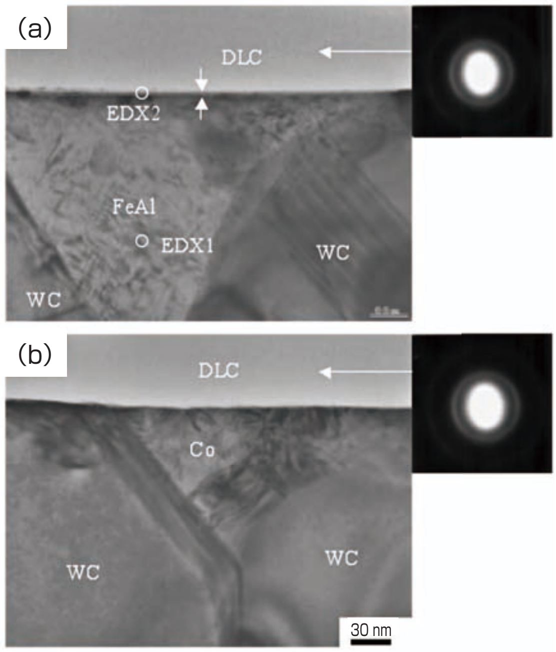

Fig. 6 Microstructure observation of the interface portion of DLC film and the WC-based hard material
(a) Interface of DLC and WC-FeAl.
(b) Interface of DLC and WC-Co.
Aluminum oxide is formed at EDX2 area of (a).

on top of the hard particles and binder phase, as shown in Fig. 6. When the boundary of the WC-FeAl and the DLC film was observed microscopically, a thin layer was observed in the boundary. When this layer was analyzed carefully, it was found that an aluminum oxide film was formed, and this was thought to increase the oxidation resistance at high temperature. This thin layer formed at approximately room temperature and was found to improve adherence to the DLC film. When the DLC film is formed on the surface of WC-FeAl hard material, it is expected to increase the mold release characteristics of the formed material. In fact, the WC-FeAl die whose the surface was coated with DLC reduced the force that was necessary for blanking of Mg foil and Cu foil.

In the WC-FeAl hard material fabricated by the developed process, the crystal growth of the WC particle, which was known to be a problem in the conventional cemented carbide, was hardly observed during sintering. In addition, there was no formation of a composite carbide phase such as the W_3Fe_3C that is known to be a brittle phase. In the early stage of the development, we did consider these results closely as these were considered to be the result of low-temperature sintering. However, some researchers are beginning to investigate the effect of Al from an academic aspect, and it is necessary to examine further the interaction between the carbides and the FeAl intermetallic compounds. As we devoted most of our efforts towards practical use, there is a lack of academic considerations, and we intend to investigate this further through joint researches with universities.

By using a hard material FeAl as the binder phase, it was possible to reduce the amount of tungsten carbide whilst attaining the same hardness, and it is thought that the use of the WC-FeAl hard material will result in tungsten-saving technology. However, there is only a little reduction effect of the tungsten by this method. A hard particle other than tungsten carbide must be composited to further reduce tungsten usage. Considering the recent rise in tungsten prices, immediate measures are highly valuable. Therefore, by using the fabrication process of WC-FeAl, we investigated the compositing of titanium hard particles and FeAl. We attempted the development of a hard material in which titanium boride particles with high heat conductivity were bound with Fe-Al intermetallic compound[12][13]. The obtained TiB_2-20 mass% (Fe-Al) sintered compact had more than 95 % of the theoretical density. While its hardness changed according to the Fe:Al ratio, it was over 1500 Hv. Since the sintering property of the TiB_2 particle was good when the Fe content of the binder phase was high, the Fe-Al intermetallic compound with high Fe content was used. In addition, the TiC-30 mass% TiB_2-30 mass% (Fe-Al) hard material, in which the titanium carbide and titanium boride particles were used as hard particles and Fe-Al intermetallic compound was used for the binder phase, showed heat conductivity of 30 W/mK, and had intermediate value between the conventional cemented carbide and cermet (TiC-Ni alloy). As various additional uses are found for cemented carbide in which the WC is bound by the FeAl intermetallic compound, we anticipate that new uses will be found for the TiB_2-(Fe-Al) or TiC-TiB_2-(Fe-Al) hard materials. In fact, the TiB_2-(Fe-Al) hard material is lighter than cemented carbide, and new applications to wear-proof parts can be considered by further evaluating the abrasion resistance.

6 Summary

Herein, we describe details concerning the development of a WC-FeAl hard material with excellent resistance in AIST, and explain the R&D from the basic research to *Type 2 Basic Research* undertaken in our research group. Figure 7 shows the schematic diagram of the course of the development. It can be seen that the current WC-FeAl was created as a result of the fusion of various elemental technologies over

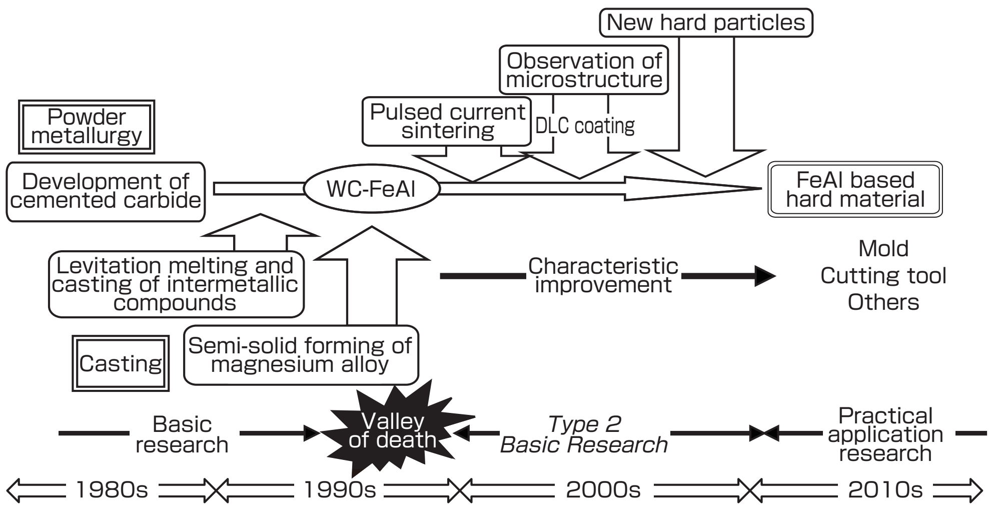

Fig. 7 Development process of WC-FeAl hard material

time. When the development of the hard material began, we aimed to replace some uses for cemented carbide, and it was clear that the outlet would be molds and cutting tools. Fortunately, the researcher who discovered this material had prior experience with cemented carbide in industry, and we were able to set the goal toward its realization relatively easily. It was difficult to achieve the targeted values using the conventional cemented carbide manufacturing process of the original hard material developed by AIST, but we were able to solve the issues steadily through the addition of new perspectives of researchers who were not directly involved in cemented carbides. However, the achievement of the target values did not lead to immediate practical utilization. By consistently transmitting the information at academic conferences for hard materials and by obtaining advice from the companies, we were able to find issues that brought us closer to realization. As a project for realizing this developed material, we obtained support from the Regional Consortium and the Strategic Core Industry Advancement Support Project (Support Industry) of the Ministry of Economy, Trade and Industry. Currently we are undertaking work towards realization through a collaboration of industry-academia-government, in addition to working towards establishment as a business. In the future, while the price increase of cobalt and its effects on the human body continue to cause concern for cemented carbides, further use can be expected due to the advancement of this development. The systems for supplying large and complex shaped members are being established, and we shall be able to provide samples to companies that are interested in this material. Our researchers are uniting to provide useful industrial material in the form of new hard materials featuring our WC-FeAl material.

References

[1] K. Kobayashi, K. Miwa and Y. Sakaguchi: Cemented carbide with high hardness and excellent oxidation resistance property (Kokodo de taisankasei ni sugureta chokogokin), Patent No. 2611177 (in Japanese).

[2] K. Kobayashi and K. Ozaki: Low-temperature formation method of aluminide intermetallic compound (Aruminaido kinzokukan kagobutsu no teiondo seikei gosei ho), Patent No. 2818860 (in Japanese).

[3] K. Kobayashi and K. Ozaki: Synthesis of aluminide intermetallics in low temperature using mechanical alloying process, *Mater. Trans., JIM*, 37, 738-742 (1996).

[4] K. Kobayashi and K. Sakazaki: Forming of FeAl intermetallic compound with Al liquid, *Funtai Oyobi Fummatsu Yakin (Journal of the Japan Society of Powder and Powder Metallurgy)*, 42, 1247-1251 (1995) (in Japanese).

[5] K. Kobayashi, K. Miwa, M. Fukunaga and M. Machida: Preparation of cemented carbide with Fe-Al binder phase, *Funtai Oyobi Fummatsu Yakin (Journal of the Japan Society of Powder and Powder Metallurgy)*, 41, 14-17 (1994) (in Japanese).

[6] M. Fukunaga, M. Machida, K. Kobayashi and K. Ozaki: Preparation of cemented carbide with FeAl binder phase by pulsed current sintering process, *Funtai Oyobi Fummatsu Yakin (Journal of the Japan Society of Powder and Powder Metallurgy)*, 47, 510-514 (2000) (in Japanese).

[7] A. Matsumoto, K. Kobayashi, K. Ozaki and T. Nishio: Fabrication of FeAl-WC Composite Using Mechanical Alloying, *Funtai Oyobi Fummatsu Yakin (Journal of the Japan Society of Powder and Powder Metallurgy)*, 48, 986-989 (2001) (in Japanese).

[8] A. Matsumoto, K. Kobayashi, T. Nishio, K. Ozaki and S. Tada: Fabrication of FeAl-WC by combustion synthesis and the mechanical properties, *Euro PM2004 Conference Proceedings*, 3, 641-645 (2004).

[9] K. Kobayashi, A. Matsumoto and K. Ozaki: Mechanical characteristic of WC-20 mass% Fe_3Al mixture synthesized by short-term mechanical alloying, *Funtai Oyobi Fummatsu Yakin (Journal of the Japan Society of Powder and Powder Metallurgy)*, 49, 284-289 (2002) (in Japanese).

[10] K. Kobayashi, A. Matsumoto, T. Nishio and S. Yasui: Change in binder phase of 75 vol% WC-FeAl mixture prepared by milling of elementary powders during pulsed current sintering, *Funtai Oyobi Fummatsu Yakin (Journal of the Japan Society of Powder and Powder Metallurgy)*, 54, 269-273 (2007) (in Japanese).

[11] K. Kobayashi, K. Ozaki, S. Tada, T. Nishio and S. Yasui: Effects of WC particle size and the FeAl amount on mechanical property of WC-FeAl hard metal, *Funtai Oyobi Fummatsu Yakin (Journal of the Japan Society of Powder and Powder Metallurgy)*, 55, 593-598 (2008) (in Japanese).

[12] K. Kobayashi, A. Matsumoto, K. Ozaki and K. Kikuchi: Fabrication of TiB_2-20 mass% Fe_3Al cermet using by mechanical alloying process, *Funtai Oyobi Fummatsu Yakin (Journal of the Japan Society of Powder and Powder Metallurgy)*, 53, 58-61 (2006) (in Japanese).

[13] H. Nakayama, K. Kobayashi, K. Ozaki, S. Tada and H. Mikami: Characteristics of TiB_2 added TiC-(Fe-Al) cermets fabricated by pulse current sintering, *Funtai Oyobi Fummatsu Yakin (Journal of the Japan Society of Powder and Powder Metallurgy)*, 56, 775-779 (2009) (in Japanese).

Authors

Keizo Kobayashi

Obtained master’s degree at the Department of Metallurgy, Graduate School of Engineering, Osaka University in March 1986. Initially joined Kobe Steel, Ltd. and then moved to the Nagoya National Industrial Research Institute, Agency of Industrial Science and Technology in 1989. Research interests include levitation melting and casting for titanium alloys, semi-solid forming technology for magnesium alloys, and non-equilibrium powder synthesis technology by mechanical alloying. Doctorate (Engineering) obtained at Osaka University in July 1997. Leader of Phase Engineering for the Processing Group, Institute of Structural and Engineering Materials, AIST in April 2001. Leader of Phase Engineering for the Advanced Material Group, Material Research Institute for Sustainable Development from April 2004. In this disclosure, developed the WC-FeAl hard material using experience with cemented carbides, obtained the patent, proposed the overall plan, and managed the research.

Kimihiro Ozaki

Obtained doctorate (Engineering) at the Department of Production Process Engineering, Graduate School of Engineering, Osaka University in March 1994. Joined the Nagoya National Industrial Research Institute, Agency of Industrial Science and Technology in 1994. Engaged in the development of magnesium amorphous alloys by mechanical alloying and pulsed current sintering, and in clarifying the basic mechanism of pulsed current sintering. In this disclosure, expanded the research into use as molds and developed the current sintering technology.

Akihiro Matsumoto

Doctorate (Engineering) obtained at the Department of Metallurgy and Department of Iron and Steelmaking, Graduate School of Engineering, Nagoya University in March 1992. Joined the Nagoya National Industrial Research Institute, Agency of Industrial Science and Technology in April 1992. Engaged in the development of high melting point structural intermetallic compounds, the synthesis of titanium amorphous and quasi-crystal alloys and energy use, and the development of environmentally-friendly cemented carbides. Leader of Structural Control Research Group, Material Research Institute for Sustainable Development in 2007. In this disclosure, expanded the results into use as cutting tools, and developed the DLC coating technology based on microscopic structure observation.

Hiroyuki Nakayama

Doctorate (Engineering) obtained at the Department of Functional Materials Engineering, Graduate School of Engineering, Toyohashi University of Technology in March 2004, followed by post-doctoral positions at the University of Washington and the Nagoya Institute of Technology. Joined AIST in April 2008. In this disclosure, developed the compositing and mixing technologies of various hard particles and Fe-Al intermetallic compounds to expand the research to tungsten-saving technology.

Discussions with Reviewers

1 Market scale of cemented carbides and effect of cobalt free product

Comment (Norimitsu Murayama, Advanced Manufacturing Research Institute, AIST)

To have the readers from different fields appreciate the economic significance of cemented carbide and the effect of achieving cobalt free hard material as the background of your research, I think you should numerically present the market scale of cemented carbide, share of Japan, and economic effect of achieving cobalt free.

Answer (Keizo Kobayashi)

According to the statistics of the Japan Cemented Carbide Tool Manufacturers Association, the domestic production of cemented carbide in FY 2007 grew to over 350 billion yen. Although it decreased after the Lehman Shock, a market scale of over 200 billion yen is maintained, and has since increased. In the international share of cemented carbide, Japan's Mitsubishi Material Corporation and Sumitomo Electric Industries, Ltd. follow Sandvik AB, Kennametal Inc., and Iscar Ltd. However, we were unable to obtain accurate figures for the share of the Japanese companies. For the effect of cobalt free, along with the cost reduction of the raw material (in raw material price, compared as reagents, the iron and aluminum powders are less than 1/4 of cobalt powder), certain aspects, such as the environmental concerns (carcinogenic issues) and the application to new high-temperature uses, are difficult to express numerically. As you indicated, we added and modified the text to include the figures where we could. The forging mold that we are developing from *Type 2 Basic Research* to application research has a market potential of about 15 billion yen (source from the Materials Process Technology Center).

2 Originality of the research

Comment (Norimitsu Murayama)

The number one originality of this research is to use Fe and Al instead of Co as the binder phase of cemented carbide. Al is used as the binder phase in the liquid state during sintering, and FeAl is synthesized to work around the disadvantages of Fe and Al. I think the paper will mature by explaining this point in chapters 2 or 3. The second originality is that you found that if both Fe and Al are in liquid form, Al evaporates rapidly and the synthesis does not go well, but when only Al become liquid, it functions as the binding agent and the synthesis of FeAl will progress. This is an example where the result did not go as in the scenario designed by thought experiment, but a way opened by patiently conducting experiments.

I think you can communicate the dynamism of the material research to the readers if you divide "3 Research scenario to realize the goal" into the scenario design by thought experiment and the changes in scenario after the actual experiments.

Answer (Keizo Kobayashi)

As you have understood, the greatest characteristic of this research was the use of Fe and Al instead of Co. Al is melted during sintering, and the target intermetallic compound is synthesized by subsequent heating. I added this point to chapter 2. In addition, I think by what process the WC-FeAl alloy is fabricated is very important in this research. While we were developing the material by following the concepts of the conventional cemented carbide, we were unable to synthesize stable materials, even though we could clarify the properties of the materials. Afterwards, we did some alternative thinking, and various secondary effects were found by reviewing the process. As a result, we were able to advance the research greatly. I added the points that you indicated and modified the "3 Research scenario to realize the goal". However, since I was unable to discern the extent to which the thought experiment would cover, I intentionally did not use the word "thought experiment".

3 Time needed for material development

Comment (Norimitsu Murayama)

Material development takes a long time. This is one characteristic of material development. Why don't you add a time axis to the development of WC-FeAl hard material in Fig. 7, and add some explanation in the text?

Answer (Keizo Kobayashi)

As you indicated, I think the addition of the time axis will be effective in enabling readers understand the progress of the material. However, in practice, the technological developments progressed side by side, and I feel it is difficult to present an exact time axis. Though very rough, I added a time axis in units of decades to Fig. 7 to emphasize that long time was needed for the material development.

4 Selection of elemental technologies for practical utilization

Comment (Hisao Ichijo, Tsukuba Center, Inc.)

This is a description of a series of processes from the need of R&D, the material synthesis, the evaluation of properties, and the development of new hard material through fusion research. The process of selection and integration of the elemental technologies is important in *Type 2 Basic Research*, and I think it will help the understanding if you explain the selection process.

Answer (Keizo Kobayashi)

As you indicated, I added a brief explanation of the selection of the elemental technologies. For the topics for the material and the process of considering its use as the mold material, I got the idea from hearing the comments of the private companies at the academic conferences.

In high-tech manufacturing, we focused on the medium to high-temperature mold as an outlet. Using the WC-FeAl hard material, for which we have been evaluating the basic properties (mechanical properties, oxidation resistance, wear test, etc.), we conducted experiments for creating material of significant size to fabricate a mold that can be used industrially, for the usability of conventional cemented carbide processing to evaluate the machining cost, and for the evaluation of cracks and oxidation by repeated heating and cooling. These items were selected by talking to the companies that showed interest in this material at academic conferences (Japan Society of Powder and Powder Metallurgy). I added and modified the text to clarify the background.

5 Effect of pulsed current sintering

Question (Norimitsu Murayama)

Please tell us the effect of the pulse current sintering. If the process involves forming at low temperature range of 660 ºC and combustive synthesis reaction that is followed by sintering, isn't it possible to fabricate the target hard material by ordinary pressure sintering?

Answer (Keizo Kobayashi)

Using the basic idea in this process (forming by molten aluminum, combustive synthesis reaction, and sintering), I think for small compacts, it can be done by a process in which heating and pressing can be done simultaneously, as in the hot press. However, for large compacts, external heating using a heater as in a hot press causes temperature differences between the area near the heater and the central part of the compact. This causes a time lag in the production of the liquid phase of aluminum and the following combustive synthesis reaction, and it would be difficult to fabricate an even sintered compact. This is a finding that we made during semi-solid forming; in pulsed current sintering, the current goes inside the compact allowing Joule heating between the powders, and this controls the occurrence of temperature difference compared to the external heating method. As a result, I believe we were able to fabricate a sintered compact without cracks, as the Al liquid phase acted evenly as a forming additive in the fabrication of the large WC-FeAl sintered compact.