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# Japan Report

SCIENCE AND TECHNOLOGY

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25 March 1986

# JAPAN REPORT

## SCIENCE AND TECHNOLOGY

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## AEROSPACE SCIENCES

### ROLLOUT OF XT-4 INTERMEDIATE CLASS TRAINING AIRCRAFT

Tokyo AEROSPACE JAPAN in Japanese Jun 85 pp 31-33

[Text] First Flight in July

On 17 April the DATRDI (Defense Agency Technical Research and Development Institute) and KHI (Kawasaki Heavy Industries, Ltd.) carried out the rollout of an XT-4 intermediate class training aircraft at KHI's Gifu Factory. Representatives of the TRDI, ASO (Air Staff Office), manufacturers, etc., participated in this event which commemorated the completion of this high-performance training aircraft produced entirely in Japan. This aircraft has a white airframe with blue stripes; its nose, tail units, and wing tips are red. Although the color of the aircraft is different from the standard color of training aircraft of the ASDF (Air Self-Defense Force), the aircraft is scheduled to fly as is until tests have been completed.

Hamada, assistant director general for air development of the TRDI: Kurosawa, ASDF colonel and chief of this project, and other staff explained rollout of the XT-4 No 1 prototype aircraft at a press conference.

1. The development of the XT-4 was carried out on schedule, and today its rollout was held. Later, the work of matching its engine and airframe will begin and the airframe will be subjected to functional tests for approximately 3 months. After that, it is scheduled to make its maiden flight in July. It will then be subjected to in-house tests by KHI until November, and it will be delivered to the Defense Agency and will be tested for 2 years by the APW (Air Proving Wing) of the ASDF. Its scheduled completion is set for 2 years.

2. Since 1981, the TRDI has developed this intermediate class training aircraft with the idea of improving the flight training system of the ASDF. Although the XT-4 is a training aircraft, and is scheduled to be used for flight training, etc., it is an excellent aircraft possessing performance and characteristics suitable for Japan's needs.

In October 1981, its basic design work was set about by KHI, MHI (Mitsubishi Heavy Industries, Ltd.) and FHI (Fuji Heavy Industries, Ltd.), cooperatively under TRDI instructions. In fiscal 1982, they carried out the design work, in fiscal 1984, they completed the manufacturer's drawing, and simultaneously, since fiscal 1983, they have manufactured four prototype aircraft and two strength test aircraft. After the No 4 (final) prototype aircraft is delivered to the Defense Agency in June 1986, the aircraft will be tested.

3. After the No 1 prototype aircraft is subjected to various tests on the ground, it will be subjected to in-house flight tests in July, then will be delivered to the Defense Agency in December for engineering and service tests. The other three prototype aircraft are scheduled for delivery to the Defense Agency in February, April and June 1986.

#### Simultaneous Development of Airframe and Engine

Although the overall length of the XT-4 aircraft is 1.5 meters longer than that of the T-33, its wingspan is slightly shorter. Although the XT-4 is a twin-engine aircraft, its airframe weight is approximately 1.3 tons lighter than that of the T-33.

#### Characteristics of the XT-4

The XT-4 is a training aircraft whose airframe and engine are developed and produced solely in Japan. Kaiser type HUD's (head-up displays) are produced under license by Shimadzu Seisakusho, Ltd., and stencil SIIIS ejection seats are being produced by Dysel. These seats and canopy blasting systems are being tested at a facility in Hurricane Mesa, Utah.

#### Wide Flight Range

The XT-4 training aircraft possesses excellent flight characteristics at a wide variety of speeds. It is equipped with new transonic wings, and the shape of its airframe has been modified.

For this reason, the XT-4 can meet qualifications necessary for flight training courses both elementary and advanced. Its fuselage has a shape to which the area rule is applied. A cross-section of its front fuselage shows circularity. The reason the vertical tail is high is so that the aircraft can withstand high-level training flights, including spin training.

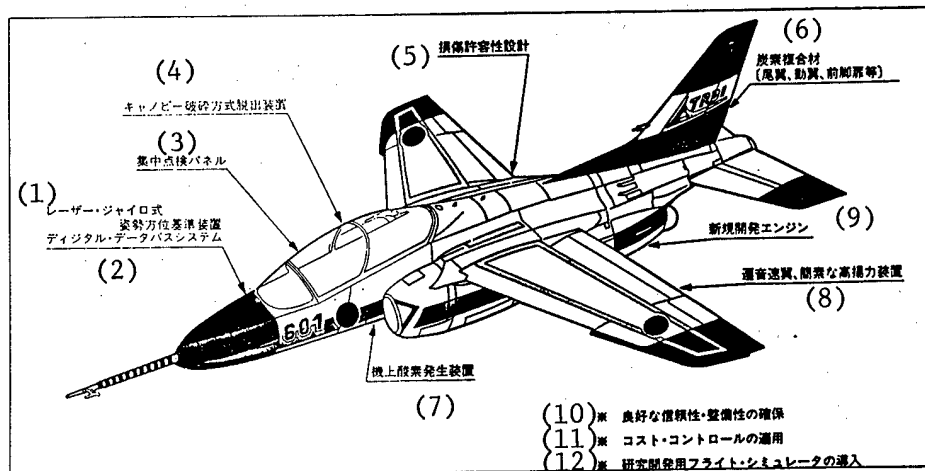
Compared with recent European training aircraft, the XT-4 is outstanding with respect to rate (10,000 feet per minute) of climb and range performance (about 700 NM).

#### Economy

The XT-4 has been developed keeping in mind cost control and the economy.

#### Application of High Technologies

The following high technology innovations have been adopted in the XT-4 intermediate class training aircraft for use before and after the 1990's.



### Structure and Features of XT-4 Trainer

#### Key:

1. Laser gyro-system attitude azimuth standard equipment
2. Digital data bus system
3. Central access panel
4. Canopy blasting system bail-out equipment
5. Scratch damage permissible design
6. Carbon composite materials (tail unit, rotor blade), nose landing gear door, etc.)
7. Airborne oxygen generator
8. Super critical wing and simple high-lift device
9. Newly developed engine
10. Ensuring of favorable reliability and maintainability
11. Use of cost control
12. Introduction of flight simulator for research and development

- (1) Use of a large amount of carbon based composite materials
- (2) Adoption of canopy blasting system bail-out equipment
- (3) Adoption of an airborne oxygen generator
- (4) Adoption of a carbon brake
- (5) Adoption of a digital data bus system
- (6) Adoption of a laser gyro-system attitude azimuth as standard equipment
- (7) Adoption of damage allowable design

## Excellent Reliability and Maintainability

High technology has been incorporated in various pieces of equipment. Reliability and maintainability have been increased by the use of access doors and simplifying the installation and removal of engines. For example, the XT-4 is designed so that the mechanic's eye is at the same level as the electronic bay while standing on the ground.

## Pursuit of Safety

As shown below, extreme care is taken with regard to safety measures considering that unskilled student pilots will control the XT-4.

- (1) Twin-engines are used in the XT-4.
- (2) The adoption of a canopy blasting system bail-out equipment will enable pilots to quickly and readily bail out in case of emergency.
- (3) Hydraulic and control systems are doubled.
- (4) Precautions against lightening striking the plane have been taken.
- (5) The aircraft is equipped with a central access panel.

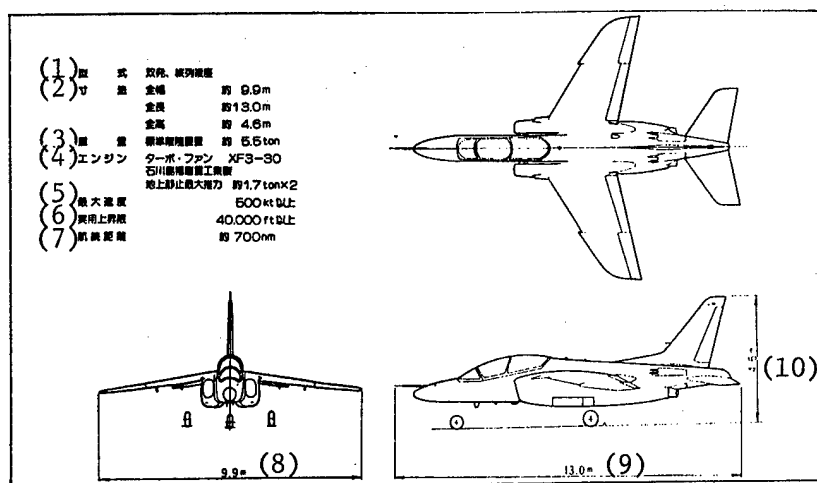
## Highest-Level Training Aircraft in the World

The XT-4 intermediate class training aircraft possesses many features which were newly designed so it can be used after the T-33 and T-1 are phased out.

Aside from performance features, efforts have been made to lighten the airframe. The XT-4 is light in weight, because carbon materials are used for the spar space of the vertical tail, aileron, rudder, speed brake, etc. As a result, the flight and range performances are enhanced.

The AHSR (air height surveillance radar) has no rotating section and unlike conventional systems in which a mechanical gyroscope is used, it has little malfunction, and high accuracy because it uses laser gyroscope.

The delivery of mass-produced aircraft will commence in fiscal 1988, and operation will begin in summer of that year. With regard to the mass production of these aircraft, KHI will be in charge of the final assembly and flight tests, as well as the front fuselage, nose, aileron and rudder. MHI will be in charge of the middle fuselage, and FHI will be in charge of the main wing, tail unit, rear fuselage, canopy and fairing. IHI (Ishikawajima-Harima Heavy Industries Co., Ltd.) will manufacture nine engines, F3-30's whose maximum ground static thrust is about 1.7 tons. On an experimental basis they will test the engines until the end of this fiscal year.



Performance Data and Three Views (Front, Side, Elevation) of XT-4 Intermediate Class Training Aircraft

Key:

1. Type: Twin-engine and longitudinal double-seat
2. Dimension: Overall width : About 9.9 meters  
Overall length : About 13.0 meters  
Overall height : About 4.6 meters
3. Weight : Standard take-off weight : About 5.5 tons
4. Engine : Turbofan, XF-3-30 made by IHI  
Maximum ground static thrust : About 1.7 tons x 2
5. Maximum speed : 500 kt or more
6. Service ceiling : 40,000 feet or more
7. Range : About 700 nm
8. 9.9 meters
9. 13.0 meters
10. 4.6 meters

The XT-4 intermediate class training aircraft has five stress points, and is designed for use in light enemy attack when necessary as well as for training. At present, no comment is being made regarding this aircraft except for its use as a trainer. However, judging from the fact that the aircraft is designed so that its airframe can withstand the strength from a maximum of 7.33 G to minus 3 G, it can probably be said that the aircraft is competitive in the world market in its performance and capability.

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## BIOTECHNOLOGY

### TRENDS IN TACTILE BIOSENSORS, SMELL-SENSITIVE BIOSENSORS

Tokyo BIO INDUSTRY in Japanese Dec 85 pp 38-45

[Article by Kohei Higuchi, Yoshie Kawana and Jun Kimura]

[Text] Biosensors, which combine substances from living organisms such as enzymes with electrochemical transducers, are thought of as a sort of taste-sensitive biosensor. Research on touch sensors has been carried out using various pressure-sensitive elements, but there have been no attempts using substances from organisms. The sense of smell is a gas sensor for the body; there are numerous uncertainties in the very meaning of "smell-sensitive biosensor," but advanced research has begun.

#### 1. Introduction

The term biosensor often indicates a sensor with a highly specialized substrate which combines a substance from living organisms, such as enzymes, with electrochemical transducers.<sup>1)</sup> But a broader sense of the term, in which biosensors copy the sensing functions of organisms whether or not substances from organisms are present, is also possible. From that perspective, a television camera can be called a sort of sight biosensor, and various pressure-sensitive elements can be called touch biosensors. A number of different electrical and mechanical touch sensors have already been proposed for applications in industrial robots.

While these tactile sensors have shown steady progress, the very concept of smell sensors is somewhat vague. Gas sensors are thought of as the most familiar example of smell biosensors, but it is difficult to produce the diverse characteristics of the sense of smell. Consequently it is conceivable that in the future it will be possible to achieve a smell biosensor by affixing living substances to gas sensors. If we compare tactile sensors and smell sensors in this light, we see that while the former have made good progress toward industrial adoption, the latter are far behind. That is because of the degree of need for each, and because tactile sensors measure physical values while gas sensors measure chemical values.

This paper is intended to describe the present state of electrical and electromechanical elements for touch biosensors, and will cite several new research projects in order to explain smell biosensors.

## 2. Tactile Sensors

### 2.1 Robots and touch sensors

The sense of touch found in the skin of animals can be subdivided into (a) a contact sense which mechanically distinguishes whether there has been contact with an object, (b) a pressure sense which perceives the amount of force applied when the object is contacted, (c) a sense of hardness which determines whether the object is hard or soft, and (d) a rubbing sense which measures tangential relative motion of the surface contacted.<sup>2),3)</sup> Therefore, a touch sensor is one which encompasses all four individual functions. They must be contact sensors, pressure sensors, hardness sensors and sliding-force sensors. How to satisfy this multifunctionality is the key to touch sensors, and the problem blocking development. Even though each individual function deals with ordinary physical measurement, touch is not a matter of measurement, and development of touch sensors is only carried out by robot researchers. This sort of narrow environment is the reason this development is very retarded, compared with such things as image sensors. But whenever the topic of robots comes up, great emphasis is always given to the necessity and desirability of touch sensors. This is clear from Harmon's 1982 tactile sensor needs survey<sup>4)</sup> and the special issue on tactile sensors of the Journal of the Japan Robot Society.<sup>5)</sup> Considering that robots are not equipped with heads, that they are expected to take over the work of humans and that a large part of human work is done with hands, the importance of tactile sensors goes without saying.

### 2.2 Distributed touch sensors

The human hand can do a very wide range of jobs, perhaps exerting great force, and perhaps grasping an egg without breaking it or doing precision work like passing a thread through the eye of a needle. This is a product of the highly developed tactile sense organs and feedback control structure of the fingers and hands.<sup>6)</sup> Physiologically, the fingers and palm of the human hand have various receptors in the dermis and epidermis which are stimulated by to external force. These receptors can be classified into four groups in accordance with field of sensitivity and speed of response to varying stimuli on the skin.<sup>7),8)</sup> But aside from those characteristics, they do not appear to be divided by the specific functions mentioned in paragraph 2.1. It is said, however, that the sharpness of the sense of touch increases with the density of these receptors. The correlation of the sharpness of the sense of touch and the density of receptors brings us the concept of distributed touch sensors.<sup>2)</sup> That is, the multiplicity of functions of touch sensors mentioned in paragraph 2.1 does not have to be present in the sensor elements; much is resolved through information processing. For example, by distributing pressure sensor elements with the same high density as in the human fingers and palm, it is possible to discriminate the spatial distribution of pressure, the integral value of weight, and even the shape of an object that is touched. It is also possible to detect rubbing information through temporal changes of spatial distribution. Sensors of this type are called distributed touch sensors.

## 2.3 Semiconductor touch sensors

In addition to single-function sensors, the distributed touch sensors mentioned in the previous paragraph have been reported as tactile sensors for robots. These are of various types, including those with arrays of microswitches or strain gauges and those using pressure-sensitive resistors like pressure-sensitive rubber or polymeric piezoelectric films such as PVDF.<sup>9)</sup> Many of these sensors have been trial-produced by robot researchers. Today's semiconductor technology is able to supply semiconductor pressure sensors with extremely high levels of performance. Distributed touch sensors have two characteristics-- increased density of sensor elements and processing of data-- and these are points at which today's semiconductor technology excels. This paragraph examines touch sensors from the perspective of semiconductor device technology.

Semiconductor touch sensors have these strong points:

- 1) Small and light high-performance arrayed sensors can be manufactured using semiconductor processor technology and silicon micromachining technology. The ability of reducing scattering between sensor elements is particularly beneficial to formation of arrays.

- (2) It is possible to place signal processing circuits on chips, and to obtain output with good signal to noise ratios. And if "intelligence" can be added, then carrying out some degree of information processing on chips will make it possible to reduce exchanges of information with the robot's controller to the necessary minimum. And bus lines to the outside can be made as few as possible to improve reliability.

There are, on the other hand, the following weak points:

- 1) Because the object is in direct contact with the surface of the element, it is necessary to protect the element from destruction or physical damage such as snapping of bonding wires. Moreover, the work of assembly is much more complex.

- 2) It is difficult to make a flexible skin like that of the human hand.

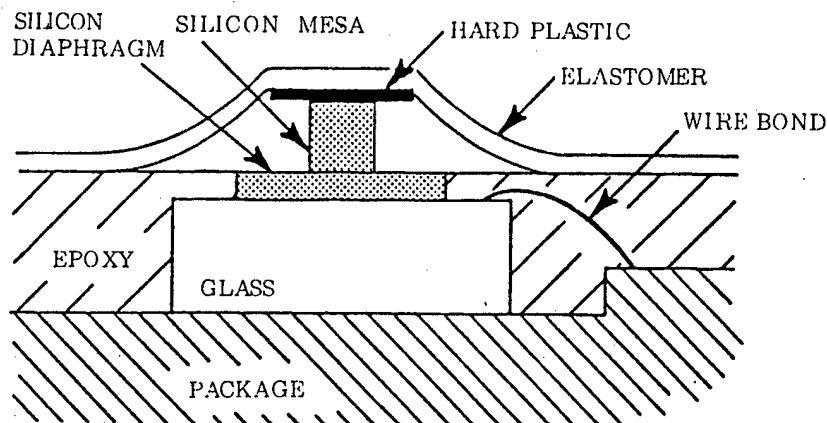
- 3) Costs are high because the elements are not suited to mass production and because the work of assembly is complex.

Representative semiconductor touch sensors are described below.

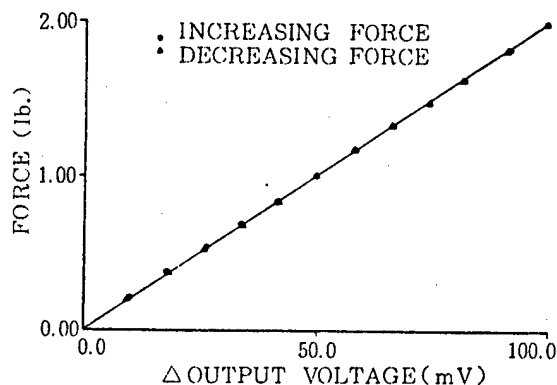
### 2.3.1 Piezo resistance element<sup>10),11)</sup>

This is an element which takes advantage of the piezoresistance effect of semiconductors. The semiconductor pressure sensors now commercially available are all of this type; they are characterized by good sensitivity and linearity. The only semiconductor touch sensor on the market is also of this type.<sup>12)</sup> This element is at present a simple pressure element; arrays have been achieved by hybridization. A cross section is shown in figure 1.

Switches for address selection during arraying of source voltage control circuits are placed on a chip, along with amplifier circuitry and piezoresistance elements by ordinary IC processes, and the surface is electrostatically attached to a glass pedestal. A depression of about 50 micrometers is etched into the center of the glass; when force is applied to the protruding piece of silicon shown in figure 1, a thin portion of silicon chip (about 100 micrometers) is deformed internally. As is clear from figure 2, the sensor is characterized by good linearity. But because the diaphragm portion of the chip is about 100 micrometers thick, sensitivity is not good.



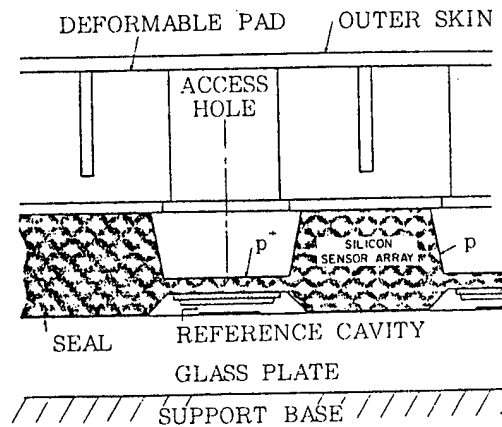
[Fig. 1] Cross section of piezoresistance element touch sensor  
An array is achieved by aligning a number of such elements.



[Fig. 2] Characteristics of piezoresistance elements  
Extremely good linearity is characteristic.  
(Note: 1 lb = 453 g)

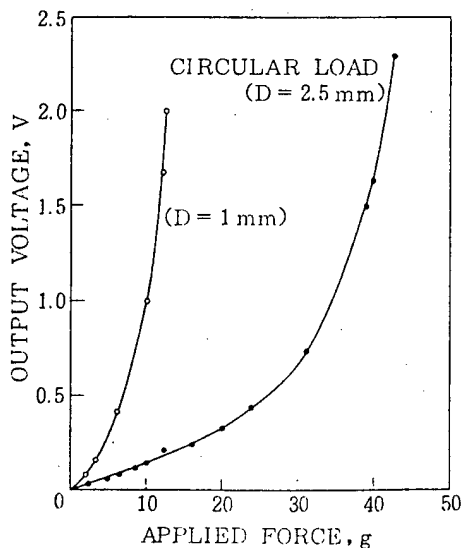
### 2.3.2 Capacitance change element<sup>13),14)</sup>

This element senses pressure as a change in capacitance; its structure is produced by aeolotropic etching of silicon, as shown in figure 3 (the dark portion of the figure is silicon). A condensor is formed in the "reference cavity" portion of figure 3, and when force is applied to the pad formed on the surface of the element, capacitance is changed when air pressure deforms the thin (10 to 20 micrometers) silicon diaphragm. Because the capacitance is inversely proportional to the gap of the cavity, the change of capacitance is not linear even if deformation of the diaphragm is proportional to the force. But the element has the advantage of extremely good sensitivity, and is suited to detection of small forces. Its characteristics are shown in figure 4. The chip has a 4 x 4 or 8 x 8 array of single elements, but no signal processing circuitry is provided at present.



[Fig. 3] Cross section of capacitance element

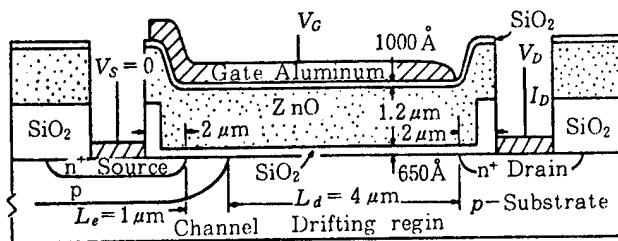
The elements of this structure are placed in a 4 x 4 or 8 x 8 array, but no signal processing circuitry is provided



[Fig. 4] Characteristics of capacitance elements  
Linearity is inferior to the piezoresistance type, but good sensitivity is characteristic.

### 2.3.3 Piezoelectric element<sup>15)</sup>

This element uses zinc oxide as a piezoelectric film in place of the silicon oxide film which makes up the normal MOS-type FET insulator film (figure 5). When force is applied to the gate portion, the piezoelectric film is polarized, and the polarization charge changes the FET's channel conductance. This pressure-sensitive element also has the advantage of extremely good sensitivity, but it can't maintain the polarization charge for long because the piezoelectric film itself leaks current; thus detection of static force is difficult.



[Fig. 5] Cross section of piezoelectric element

This is characterized by good sensitivity and the non-use of micromachining technology, as in the case of diaphragm formation. But assembly is difficult.

These are three representative semiconductor touch sensors; at present there is still none which completely provides all the strong points of semiconductor sensors stated above. In particular, signal processing is still inadequate. There are limited reports of hybrid elements with pressure-sensitive resistors placed on a silicon chip;<sup>16)</sup> further research is awaited. Touch sensors cannot be achieved without exchange between users and device technologists, but there is little such exchange in Japan; active participation on both sides is desired.

## 3. Smell-sensitive Biosensors

### 3.1 Working of the sense of smell and smell biosensors <sup>17</sup>

The sense of smell, like that of taste, is a sense which perceives by means of receptors stimulated by chemical substances. In the case of humans, sensitive cells called olfactory cells are concentrated on the roof of each nasal cavity. The olfactory cells correspond to the termini of the olfactory nerves; when an aromatic substance adheres to the receptor membrane, a change of potential is set up on the receptor membrane. This potential change on the

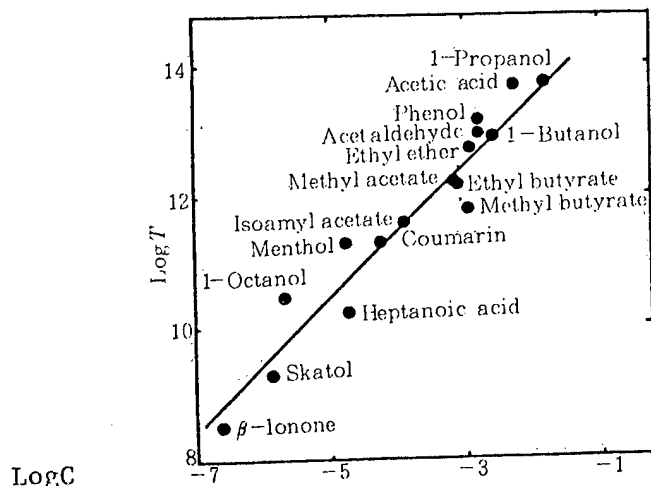
membrane generates an electrical impulse which is conveyed directly to the olfactory nerve, by which the aromatic data is transmitted. It is thus possible to call the olfactory cell a chemical-electrical transducer.

The other end of the olfactory cell forms a nonmedullated nerve, a number of which are grouped together into bundles called olfactory fibers which pass into the cranium and enter the olfactory bulbs, which are the primary central structures. As yet little is understood about the mode of information processing in the olfactory bulbs. But because the response of the individual cells, both in the epithelium and in the olfactory bulb, differs according to the type of aromatic substance, it is possible that the body discriminates smells on the basis of unique patterns.

Various sensors have been developed to measure the density of gases, but they can hardly be called adequate in terms either of sensitivity or selectivity. The development of a sensor which can distinguish and evaluate smells as a whole, rather than identifying and quantifying individual constituents, is desired. The development of a smell biosensor should be thought of as including all these points.

### 3.2 Sensors modeled on the receptor membrane

The first process in the sense of smell is thought to be adsorption of the aromatic substance on the receptor membrane and the accompanying change in membrane electric potential. Kuwahara et al. discovered, using a monomolecular film of lipid extracted from bovine nasal epithelium, that the surface tension changed in response to aromatic substances (figure 6).<sup>18)</sup> And because aromatic substances cause a change in membrane electric potential even in cells other than olfactory cells (mouse neuroblasts, clone N-18), it is thought that adsorption of aromatic substances does not involve a unique receptor protein, but rather the hydrophobic region of the body's membranes.<sup>19)</sup>



[Fig. 6] Plot of concentration C of chemical substance which causes 10 dyne  $\text{cm}^{-1}$  increase in surface tension of monomolecular film of lipid extracted from bovine nasal epithelium against concentration T at which that chemical substance is discernable to humans.<sup>18)</sup>

Tests have been made of a number of sensors which make use of adsorption of various chemicals by tissue substances. Thompson et al. tested sensors in which functional substances maintained on a bimolecular lipid film responded to chemical substances.<sup>20)</sup> But stable use of these sensors over a long period was difficult.

There have also been reports of gas sensors with tissue substances built up on a substrate using Langmuir-Blogett film (L-B film) methods. Baker et al.<sup>21)</sup> and Tredgold et al.<sup>22)</sup> tested sensors reacting NO<sub>2</sub> against copper phthalocyanine and porphyrin respectively. Although these sensors still have problems, including response time, they are extremely sensitive, and further research is anticipated.

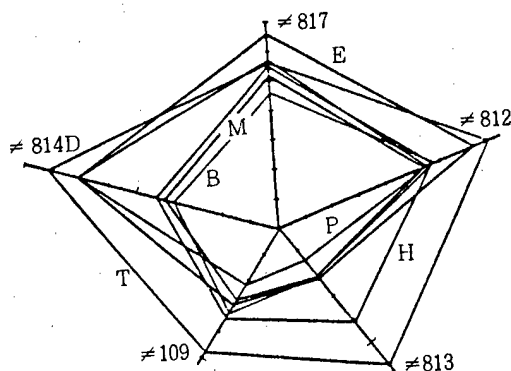
### 3.3 Sensors which discriminate among aromatic substances

There are uncounted aromatic substances, which are "foreign matter" to the body. The sense of smell discriminates among these, and makes comprehensive judgments and evaluations. As stated above, it is thought this discrimination is done through recognition of patterns of responses of groups of cells with differing characteristics. Consequently, there have been attempts to discriminate chemical substances by preparing a number of sensors with differing characteristics, and comprehensively judging their outputs.

Seta et al. equipped a test box with five different semiconductor gas sensors and measured the individual sensors' responses to aromatic gases. A single gas was prepared in two different concentrations (C<sub>1</sub>, C<sub>2</sub>) which were injected into the test box, at which time the resistance values (R<sub>1</sub>, R<sub>2</sub>) were measured. Then the discrimination constant alpha of each sensor was calculated with the formula:

$$\alpha = \frac{\log R_2 - \log R_1}{\log C_2 - \log C_1}$$

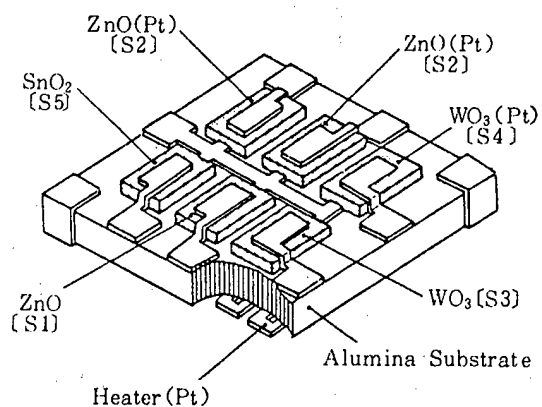
The five alpha values for single gases were plotted on five axes as in figure 7, and the resulting patterns used to discriminate the aromatic substances.



[Fig. 7] Graph of discrimination index of aromatic substances for five sensors<sup>23)</sup>  
 E: ethyl ester, M: methanol, B: benzene, T: trichloroethane, H: normal heptane, P: pyridine

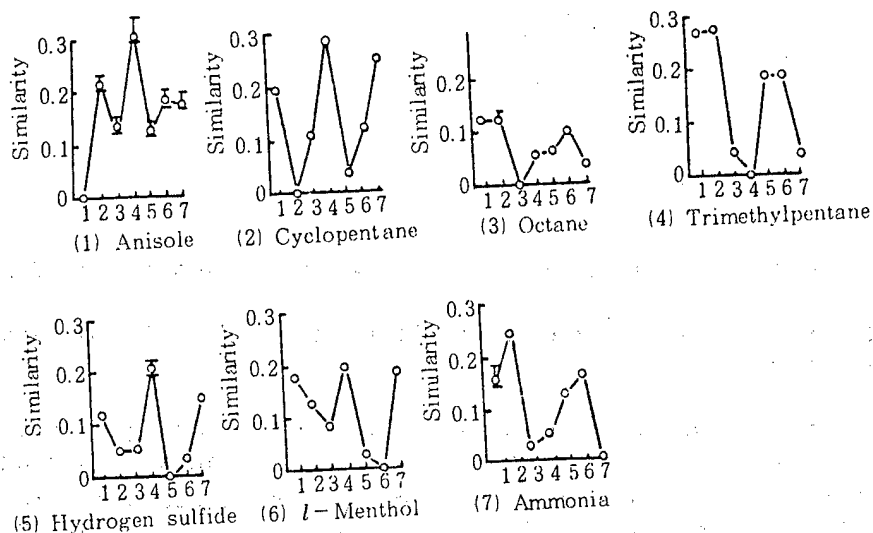
Kaneyasu et al. have reported a smell sensor consisting of thick film gas sensors using six different materials integrated on an aluminum substrate, as shown in figure 8.<sup>24)</sup> The responses from individual sensors were detected as unique patterns corresponding to the type of gas. Patterns for a number of gases were recorded in advance, and experimenters attempted to identify gases by evaluating, as distance  $d$  in Euclidian space using formula (1) below, the degree of similarity between prerecorded pattern  $P$  and pattern  $X$  randomly detected by the sensor.  $S$  in the formula is the synapse load.

$$d = (||S(X-P)||_2)_2 \quad (1)$$



[Fig. 8] Composition of integrated sensor

The possibility of discriminating among seven different gases was examined. The similarities of detected patterns for each gas were as in figure 9; it was concluded there is no obstacle to distinguishing gases.



[Fig. 9] Similarity of aromatic substances against standard patterns

The number of olfactory cells in animals is said to be about five million per side in the case of the rabbit; it may well be impossible to completely replace their functions with some number of semiconductor sensors. Conversely, it may become possible to detect things not detected by living organisms; future developments are anticipated.

What is used most in the field of analysis for discrimination and identification of gases is the gas chromatograph. Present models are devices rather than sensors, but they may become highly reliable smell sensors if they can be miniaturized. Angell et al. have indicated that minute valves, separatory columns and detectors can be built on a two-inch silicon wafer by means of microprocessing.<sup>25)</sup>

On the other hand, there is more and more research on biosensors which make use of the capability of living organisms to distinguish elements.<sup>1)</sup> Most of these are sensors which measure the concentration of chemical substances in aqueous solutions, but a sensor that measures ammonia in the air has also been

tested. Because the sense of smell itself operates only after molecules in a gaseous state have been dissolved in mucus, it should be possible to develop various gas sensors using biosensors. Biosensors are generally highly selective, and so promise high performance, depending on intended use.

### 3.4 Olfactory Biosensor

The sense of smell can hardly be called a sense which is essential for life in today's society, and it may be unreasonable to consider an olfactory biosensor as an "artificial organ." But measurement of senses is getting much attention in some fields. The measurement of "bad smells," a matter of sense pollution, is one of these fields. Because there have been considerable discrepancies in the sense of harmfulness in measuring concentrations of individual chemical substances, organic testing laws (sense measurement laws) are being introduced. But these laws, which depend on human senses, have the shortcomings that (a) results are affected by many factors including differences between individuals, fatigue, and bodily and environmental conditions, and (b) the costs are high; sensors that make objective evaluations may well become necessary.

As life in society becomes more abundant, demands for "a pleasant environment" are expected to become stronger and stronger. Sensors for smells, including "aromas," are expected to be necessary for evaluation of such an environment.

### 4. Conclusion

The present state of research on tactile biosensors and olfactory biosensors is described above. As cautioned at the first, the use of the term "biosensors" includes not just sensors making direct application of materials extracted from organisms, such as enzyme electrodes, but also sensors which copy the senses. That is especially so in the case of touch sensors. In the case of olfactory biosensors, for which the research itself is in its infancy, the active application of substances extracted from living organisms is still an ongoing process.

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METALLURGICAL INDUSTRY

DEVELOPMENT, USES OF NEW METAL MATERIALS EXAMINED

Tokyo NIKKO MATERIALS in Japanese Aug 85 pp 89-100

[Article by J. Tada: "New Metal Materials"]

[Excerpt] 3. Development of New Metals

3-1 Superconductive Metals (Alloys)

1) What are superconductive metals (alloys)?

Superconduction is the phenomenon a certain type of metals exhibit of zero electric resistance when cooled to a temperature close to absolute zero ( $-273.15^{\circ}\text{C}$ ).

Superconduction has merits. Because of zero resistance it is possible to send large doses of high-density electric current without causing loss. Furthermore, when electricity is sent in coils, a permanent current flows without consuming power, and a strong magnetic field can be realized.

This phenomenon was discovered in 1911 by (Onnes) of the Netherlands while he was determining the electric resistance of mercury in liquid helium ( $-269^{\circ}\text{C} = 4^{\circ}\text{K}$ ).

About a half century later, in 1957, Bardeen, Cooper and Schrieffer of the United States compiled the superconductivity theory (the BCS theory, for which they received the Nobel Prize). This caused subsequent rapid development and application of superconductive metal materials which possess such superconductivity.

The temperature at which metal causes superconduction is called "critical temperature" ( $T_c$ ) and the magnetic field where superconductivity disappears is called "coercive magnetic field" ( $H_c$ ). Superconductivity is best utilized when both  $T_c$  and  $H_c$  are high.

At this moment, development is underway for superconductive metals with a low critical temperature ( $T_c$ ) and a corresponding coolant.

Table 1. History of Metal Material Technology Development

- 1911 Hardening process of Al alloy (duramin) developed during Germany's industrial age. (Onnes) of the Netherlands discovered superconductivity of mercury.
- 1917 Kotaro Honda developed KS magnet steel.
- 1923 Clapp Company invented the superhard alloy (Widia).
- 1940 Goro Kitahara and Isamu Igarashi invented super-super duralumin, which was used for the "zero fighter".
- 1942 Jet engine was developed using cobalt alloy (bitalium).
- 1945 Bell Lab discovered (Whisker).
- 1947 Titanium production by (Chroe) method was industrialized.
- 1951 Lead, et al., of the University of Illinois discovered the shape-memory property of gold/cadmium alloy.
- 1960 (Warchan) Company developed superconductive material Nb-Ti alloy. (Dewey), et al., developed the first amorphous alloy by liquid quenching.
- 1963 U.S. Navy Institute developed shape-memory alloy using nickel titanium alloy.
- 1970 Takeshi Masumoto, et al., established amorphous alloy production method by quenching.
- 1976 Kyoji Tachikawa et al., realized the world's top magnetic field of 17.5 tesla by superconductive magnet.
- 1979 Michio Yamazaki, et al., developed new alloy engineering method for super heat-resistant alloys.
- 1980 Amorphous alloys and shape memory alloys started practical use.

## 2) Types and Characteristics of Superconductive Metal Materials

Today, no less than 100 metal materials which exhibit superconductivity have been found. Those whose application seems promising are limited in number.

At present, Nb-Ti alloy and inter-metallic compounds such as  $\text{Nb}_3\text{Sn}$ ,  $\text{Nb}_3\text{Ge}$  and  $\text{Nb}_3\text{Ga}$  are considered promising. The critical temperature has at last exceeded  $20^\circ\text{K}$  so that liquid hydrogen ( $20^\circ\text{K}$ ) can be used.

Future development is expected for superconductivity metal materials in the high temperature range for which liquid neon ( $27^\circ\text{K}$ ) and liquid nitrogen ( $77^\circ\text{K}$ ) can be used. For such, alloys of three metals, Nb, Ge and Al are considered promising.

### 3) Application of Superconductive Metal Materials (such as Alloys)

Superconductive metal materials are applied to three areas: large-scale transmission of electric power, utilization of ferromagnetic fields, and semiconductor devices.

In the field of power transmission, it is possible to send a current 2000 times larger (1 million ampere per 1 cm<sup>2</sup> of cross section) than that sent using conventional normal conductivity copper cable without causing transmission loss.

Secondly, for utilization of ferromagnetic fields (superconductivity magnets), research and development is underway on linear motor cars by Japan National Railways and other institutions, also plasma containment in nuclear fusion furnaces, and MHD generation (magnetic hydrodynamics generation). Studies have also started on how to store electric power in permanent current conditions.

Thirdly, application to semiconductor devices includes the Josephson device, which is gaining attention as a promising post-silicon semiconductor. While high density integration is limited with silicon semiconductors the Josephson device with superconductivity features very small caloric generation and a power consumption 1/1000 that of silicon semiconductors.

Practical applications are still unclear.

Development of superconductive materials in Japan is being aggressively pursued by Furukawa Electric Co., Ltd.; Hitachi Cable, Ltd.; Mitsubishi Electric Co., Ltd., etc.

### 3-2 Amorphous Metals (Alloys)

#### 1) What is an amorphous metal?

Amorphous refers to a substance which is usually in a non-crystal condition. In this type of substance (represented by glass, etc.) orientation of atoms is irregular (disorderly).

Since metal substances are generally most stable when their atomic orientation is regular, it is not easy to change that into an irregular form. In the early stages of the study, methods to partially create amorphous metals by means of vacuum evaporation and non-electrical plating were developed but they did not reach the stage of practical application.

Amorphous alloys can be made by directly solidifying the liquid state of molten metals whose atomic orientation is made irregular. For this purpose, however, it is necessary to quench the material at at least 1 million °C/second. The liquid quenching development process started in the 1960s. The practical technology became feasible around 1970 with the production of amorphous alloy ribbons. Today amorphous alloys, in the form of 10cm wide tape, can be produced. Also, wire and granule forms have been developed to start diversification of the products.

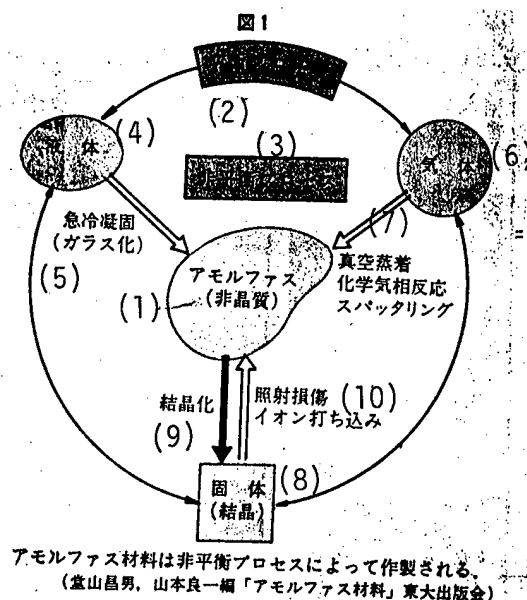


Figure 1. Amorphous Materials Made by a Non-equilibrium Process.  
(AMORPHOUS MATERIALS edited by M. Doyama and R. Yamamoto. Tokyo University Publication)

Key:

1. Amorphous materials
2. Equilibrium process
3. Non-equilibrium process
4. Liquid
5. Quench freezing (glassification)
6. Gas
7. Vacuum evaporation  
Chemical air phase reaction  
Sputtering
8. Solid (crystal)
9. Crystallization
10. Destruction by radiation  
Ion implantation

What kinds of amorphous alloys are available?

According to the Allied Corp., of the United States, which possesses the basic patent in this field, (the company's "Patent on the Basic Alloy Composition for Amorphous Alloys" was approved in Japan in November 1983), they are as follows:

The composition of amorphous alloy is expressed as  $MaYbZc$  (where M = transition metal element, Y = metalloid of light mass, and Z = metalloid) and their composition ratio is approximately a = 60-90 atom percent, b = 10-30 atom percent and c = 0.1-15 atom percent.

Specific names of the metals are shown in Table 2. Among the alloys listed, those which have been commercialized include the alloys shown in Table 3.

Recently, manufacturers have not been disclosing the composition of amorphous alloys, making it difficult to identify them. The reason is that the companies are afraid of conflicting with Allied Corp.'s basic composition patent.

## 2) Characteristics and Applications of Amorphous Alloys

It is known that amorphous alloys have various properties. These are shown in Figure 2. They are innovative metals whose wide-ranging application is considered possible because of their respective properties.

Major properties are: First, mechanical properties such as high hardness and high strength; second, high corrosion resistance which, it is said, can be made several thousand times stronger than stainless steel; third, excellent magnetic property; and fourth, high electric resistance and small temperature coefficient.

Regarding the high strength and high hardness properties cited above, those of amorphous alloys are extraordinarily high compared with polycrystal metals.

Some transition metal amorphous alloys exhibit hardness of at least 10GPa ( $1,020 \text{ kg/mm}^2$ ) and strength of 4 GPa ( $408 \text{ kg/mm}^2$ ) and are better than maraging steel which is considered the strongest of today's metal materials.

Examples of applications developed for these high-strength, high-hardness properties include as an alternative to steel belts for steel radial tires, materials for iron reinforced concrete, razor blades, etc. They are also suitable for magnetic head materials because in film form they are not easily eroded.

Taking advantage of their outstanding corrosion resistance, possible applications include electrodes for salt electrolysis, for fuel cells, as well as for solar heat absorbers.

Amorphous magnetic materials utilizing the magnetic properties of amorphous alloys are being developed in a wide-range from transformer material to electric and electronic parts. The latter is the field where their development is most advanced.

Amorphous alloys are otherwise considered most suitable as hydrogen occlusion alloys (S. Nanao, assistant professor, Tokyo University).

Amorphous alloys which show superconductivity are relatively common but none of them has yet surpassed crystal metals.

Table 2. Amorphous Alloy Component Elements

|                          |                                                                  |
|--------------------------|------------------------------------------------------------------|
| M<br>(Transition Metals) | Iron, Nickel, Cobalt, Chromium<br>Molybdenum, Vanadium           |
| Y<br>(Light Metalloids)  | Phosphorus, Carbon, Boron                                        |
| Z<br>(Metalloids)        | Aluminum, Silicon, Tin, Antimony<br>Germanium, Indium, Beryllium |

(Source: Allied Company Composition Patent)

Table 3. Examples of Amorphous Metals (Alloys)

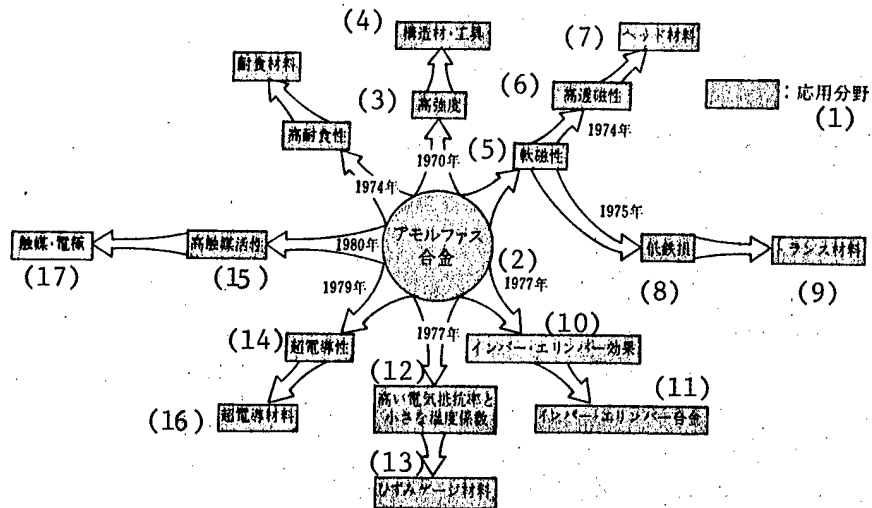
| (1) (2) |     | (3)                                                                                                                                                | (4)             | (5)                                         |
|---------|-----|----------------------------------------------------------------------------------------------------------------------------------------------------|-----------------|---------------------------------------------|
| 種 類     |     | 系 (化学組成例)                                                                                                                                          | おもな作製法          | 特 徴                                         |
| (6)     | 純金属 | Bi, Ga,<br>Fe, Ni                                                                                                                                  | 低温真空蒸着<br>(8)   | 室温以下で結晶化<br>(11)                            |
| (7)     | 合 金 | Pd <sub>80</sub> Si <sub>20</sub> , Fe <sub>80</sub> B <sub>20</sub> ,<br>Cu <sub>50</sub> Zr <sub>50</sub> ,<br>La <sub>75</sub> Au <sub>25</sub> | 急 冷 凝 固<br>(9)  | 軟磁性, 高強度, 耐食<br>性, インバー特性, 超<br>伝導特性など (12) |
|         |     | Gd <sub>80</sub> Co <sub>20</sub> ,<br>Sm <sub>30</sub> Co <sub>70</sub>                                                                           | スパッタリング<br>(10) | 垂直磁化 (バブル)<br>(13)                          |
|         |     |                                                                                                                                                    |                 | 磁気バブルメモリー<br>(14)                           |
|         |     |                                                                                                                                                    |                 | 磁気バブルメモリー<br>(15)                           |

(堂山・山本「アモルファス材料」東大出版会) (16)

## Key:

- Types
- Group (examples of chemical composition)
- Major preparation methods
- Characteristics
- Applications
- Pure Metals
- Alloys
- Cold vacuum deposition
- Rapid quenching solidification
- Sputtering
- Crystallization at below room temperature
- Soft magnetism, high strength, corrosion resistance invar properties, super-conductivity, etc.
- Vertical magnetization (bubble)
- Power transformer, magnetic head, high-strength materials, compound materials, super-conductivity materials, etc.
- Magnetic bubble memory
- (AMORPHOUS MATERIALS by Doyama/Yamamoto. Tokyo University Publication)

図2 アモルファス合金の性質と応用



(NIKKEI HI-TECH JOHO No. 14,  
Japan Economic Journal)

Figure 2. Characteristics of Amorphous Alloys and their Applications

Key:

- |                              |                                                                      |
|------------------------------|----------------------------------------------------------------------|
| 1. Application field         | 10. Inver/Elinver Effect                                             |
| 2. Amorphous alloys          | 11. Inver/Elinver Alloy                                              |
| 3. High strength             | 12. High electric resistance ratio and small temperature coefficient |
| 4. Building materials, tools | 13. Distortion gauge material                                        |
| 5. Soft magnetism            | 14. Super conductivity                                               |
| 6. High permeability         | 15. High catalytic activity                                          |
| 7. Head material             | 16. Superconductive materials                                        |
| 8. Low iron loss             | 17. Catalyst/electrode                                               |
| 9. Transformer material      |                                                                      |

### 3. Development of Amorphous Alloys and their Applied Products

As stated above, amorphous alloys with various properties are expected to have wide-ranging applications. In reality, however, only a portion of them has achieved practical application.

#### (1) Power Transformer

Presently, development is centered on power transformers and electronic equipment and parts.

Applications to power transformer iron cores is calling for consumption volumes large enough to create an attractive market.

U.S. Allied Corp. is said to be making the greatest effort in this field. Spearheaded by EPRI (U.S. Electric Power Research Institute), field studies on power distribution transformers with amorphous alloy cores are under way. 800 units were produced for this purpose and an evaluation is expected in two years. The evaluation on durability and reliability is most important because a power transformer should last 30 years.

To compete with the United States, Research Development Corporation [RDC] of Japan is developing amorphous alloy materials designed for power transformers. Commissioned by RDC, Nippon Steel Corporation is working on the trial production of 10cm-wide amorphous alloy tape for transformers.

Also, Kawasaki Steel Corporation is seriously studying mass production of amorphous alloys, mainly for transformer use.

Responding to this, transformer manufacturers such as Mitsubishi Electric Co., Ltd.; Takaoka Electric Mfg. Co., Ltd.; Osaka Transformer Co., Ltd.; and Tokyo Shibaura Electric Co., Ltd., have completed trial production of several units each of amorphous transformers, and are said to be ready to start mass production studies (NIKKEI MECHANICAL 22 April 1985, Nikkei McGraw-Hill).

## (2) Electronic Equipment/Parts

Development of electronic equipment parts and electronic materials, taking advantage of the electromagnetic properties of amorphous alloys, has been rapidly progressing.

The primary product is the magnetic head. In this field, TDK has already established the patent in the United States. Other companies such as Sony Corporation, Tohoku Metal Industries, Ltd., and Hitachi Metals, Ltd., are also advancing development.

A second concern is inductance parts for switching power. This market is rapidly expanding because of the needs of office automation equipment. To make switching power smaller in size and lighter in weight, high-frequency inductance with amorphous alloys is drawing attention. Three companies, Toshiba, Hitachi Metals, and TDK are ahead of others in this field, while Tohoku Metal is also engaged in development. Choke coil and noise filters are also commercialized by these three companies.

A third field of application involves various sensors: hydraulic sensors (using magnetostriction phenomenon of amorphous alloys) by Matsushita Electric Industrial, azimuth sensors (to be used as navigation sensors for automobiles) by Hitachi Metal, and pressure sensors by Aisin Seiki Co., Ltd., etc.

Finally, a subject which should not be ignored when reviewing the future market of amorphous alloy materials, is the issue over the patent on basic compositions of amorphous alloys claimed by U.S. Allied (application filed in 1973, patent established in 1984). Details of this issue were described earlier. In the wake of the legal judgment made last year to approve the patent, Japanese manufacturers have to take some counteraction.

Table 4. Major Applications of Amorphous Metal Materials

| Properties                      | Applications                                                                                         |
|---------------------------------|------------------------------------------------------------------------------------------------------|
| high strength materials         | tire code, concrete reinforcement, cutlery                                                           |
| soft magnetism                  | power transformer, high frequency transformer, switching regulator, motor, magnetic shield           |
| high permeability materials     | magnetic head, magnetic sensor, magnetic separation                                                  |
| magnetic film materials         | magnetic bubble memory, photomagnetic disc                                                           |
| corrosion resistance            | electrode materials, solar heat absorption plate, mole materials                                     |
| high magnetostriction materials | ultrasonic oscillator, delay line, transducer, frost sensor, pressure sensor, distortion gauge, etc. |
| others                          | hydrogen retention (occlusion) alloys, superconductivity materials                                   |

(SISCO)

Table 5. Trial Production of Transformers Using Amorphous Alloys  
(Mitsubishi Electric Co., Ltd.)

表5 アモルファス合金を用いた変圧器の試作(三菱電機)

| (1) 米 国                                                           | (2) 西暦<br>(年) | 日 本 (3)                                                                                                                                                                                                      |
|-------------------------------------------------------------------|---------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (4) WH社, EPRIと4年契約<br>[材料特性評価,<br>鉄心製造技術,<br>ハンドリング技術,<br>経済性評価]  | 1979          |                                                                                                                                                                                                              |
| (5) アライド社, 単相15kVA                                                | 1980          | ✓三菱電機, 単相500VA (9)<br>✗高岳製作所, 単相300VA (10)                                                                                                                                                                   |
| (6) GE社, 単相25kVA                                                  | 1981          | ←大阪変圧器, 単相10kVA(アライド社と共同開発) (11)<br>←高岳製作所, 単相1kVA(東京電力と共同開発) (12)                                                                                                                                           |
| (7) WH社, 10kVA 1年間の実用テスト                                          | 1982          | ←三菱電機, 3相400VA(5脚鉄心)(13)                                                                                                                                                                                     |
| (8) GE社, EPRIと3年契約<br>[単相25kVAを1000台製造,<br>設計, 製造の量産技術,<br>経済性評価] | 1983          | ←大阪変圧器, 単相30kVA (14)<br>←東芝, 単相110kVA, 3相11kVA(エバンス型) (15)<br>←日立製作所, 単相15kVA (16)<br>←高岳製作所, 単相20kVA(東京電力と共同開発) (17)<br>←三菱電機, 3相35kVA(モールド式) (18)<br>←日立製作所, 単相20kVA (19)<br>←東芝, 3相100kVA(5脚鉄心, 油入り) (20) |

(「日経メカニカル」1985年4月22日号, 日経マグロウヒル社) (21)

Key:

1. United States
2. Years
3. Japan
4. (Westinghouse) concludes 4-year contract with EPRI  
Material property evaluation  
Iron core production technology  
Handling technology  
Economic evaluation
5. Single phase 15kVA by Allied
6. Single Phase 25kVA by GE
7. WH company conducts one year application test of 10kVA
8. GE company concludes 3-year contract with EPRI  
Production of 1000 units of single phase 25kVA  
Mass production technology for designing/manufacturing  
Economic evaluation
9. Single phase 500VA by Mitsubishi Electric Co., Ltd.
10. Single phase 300VA by Takaoka Electric Mfg. Co., Ltd.
11. Single phase 10kVA by Osaka Transformer Co., Ltd.  
(co-development with Allied)

[Key continued on following page]

12. Single phase 1kVA by Takaoka Electric Mfg. Co., Ltd.  
(co-development with Tokyo Electric Co., Ltd.)
13. 3 phase 400VA by Mitsubishi Electric Co., Ltd. (5 leg iron core)
14. Single phase 30kVA by Osaka Transformer Co., Ltd.
15. Single phase 10kVA, 3 phase 1kVA (Evans type) by Toshiba Co., Ltd.
16. Single phase 15kVA by Hitachi
17. Single phase 20kVA by Takaoka Electric
18. 3 phase 35kVA (mold system) by Mitsubishi Electric
19. Single phase 20kVA by Hitachi, Ltd.
20. 3 phase 100kVA (5 leg iron core, oil included)
21. (NIKKEI MECHANICAL 22 April 1985, Nikkei-McGraw-Hill)

Table 6. Amorphous Alloy Materials by Japan Amorphous Metals (Allied Corp.)

表6 日本非晶質金属(米・アライド社)のアモルファス合金材料

(1) アモルファス合金 磁性材

| (2) 銘柄   | (3) 組成(原子%)                                                                               | (4) 主な用途                |
|----------|-------------------------------------------------------------------------------------------|-------------------------|
| 2605SC   | Fe <sub>81</sub> B <sub>13.5</sub> Si <sub>3.5</sub> C <sub>2</sub> (5)                   | パルストランス、センサー、電力用トランス    |
| 2605S-2  | Fe <sub>78</sub> B <sub>13</sub> Si <sub>9</sub> (6)                                      | 配電用変圧器、チョークコイル、電力用変圧器   |
| 2605CO   | Fe <sub>67</sub> Co <sub>18</sub> B <sub>14</sub> Si <sub>1</sub> (7)                     | 航空機用電源トランス、パルストランス、センサー |
| 2605S-3A | (8)                                                                                       | SMPSトランス<br>シグナルトランス    |
| 2826MB   | Fe <sub>40</sub> Ni <sub>38</sub> Mo <sub>4</sub> B <sub>18</sub> (9)                     | 小型シグナルトランス、<br>磁気シールド   |
| 2605SM   | Fe <sub>73.5</sub> Ni <sub>4</sub> Mo <sub>3</sub> B <sub>17.5</sub> Si <sub>2</sub> (10) | SMPSトランス<br>シグナルトランス    |
| 2705M    | Co <sub>65</sub> FeNiMoBSi (11)                                                           | 磁気ヘッド、センサー              |

(12) アモルファス合金 Ni基ろう付箔

| (13) 銘柄 | (14) 公称組成(wt%)                                                                                        | (15) 相当AWS | ろう付温度(°C) | (16) |
|---------|-------------------------------------------------------------------------------------------------------|------------|-----------|------|
| MBF-15  | Ni <sub>81</sub> Cr <sub>13</sub> Fe <sub>4.2</sub> Si <sub>4.5</sub> B <sub>2.8</sub>                | —          | 1175      |      |
| MBF-17  | Ni <sub>81</sub> Cr <sub>11.3</sub> W <sub>8</sub> Fe <sub>4</sub> B <sub>2.2</sub> Si <sub>1.5</sub> | —          | 1175      |      |
| MBF-20  | Ni <sub>81</sub> Cr <sub>7</sub> Fe <sub>3</sub> Si <sub>4.5</sub> B <sub>3.2</sub>                   | BNi-2      | 1040      |      |
| MBF-30  | Ni <sub>81</sub> Fe <sub>14.5</sub> B <sub>3.2</sub>                                                  | BNi-3      | 1040      |      |
| MBF-35  | Ni <sub>81</sub> B <sub>2.2</sub> Si <sub>7.3</sub>                                                   | —          | 1020      |      |
| MBF-50  | Ni <sub>81</sub> Cr <sub>18.5</sub> Si <sub>7.5</sub> B <sub>1.4</sub>                                | BNi-5      | 1175      |      |
| MBF-60  | Ni <sub>81</sub> P <sub>11</sub>                                                                      | BNi-6      | 980       |      |
| MBF-65  | Ni <sub>81</sub> Cr <sub>14</sub> P <sub>10</sub>                                                     | BNi-7      | 980       |      |
| MBF-75  | Ni <sub>81</sub> Co <sub>23</sub> Cr <sub>10</sub> Mo <sub>7</sub> Fe <sub>5.5</sub> B <sub>3.5</sub> | —          | 1205      |      |
| MBF-80  | Ni <sub>81</sub> Cr <sub>15.2</sub> B <sub>4</sub>                                                    | —          | 1175      |      |
| MBF-90  | Ni <sub>81</sub> Co <sub>20</sub> B <sub>2.7</sub> Si <sub>4</sub>                                    | —          | 1130      |      |

(17) アモルファス合金 Cu基ろう付箔

| (18) 銘柄 | (19) 公称組成(wt%)                                                          | ろう付温度 | (20) |
|---------|-------------------------------------------------------------------------|-------|------|
| 2002    | Cu <sub>78.3</sub> Ni <sub>9.9</sub> Sn <sub>4.0</sub> P <sub>7.8</sub> | 660°C |      |
| 2005    | Cu <sub>77.6</sub> Ni <sub>5.7</sub> Sn <sub>9.7</sub> P <sub>7.0</sub> | 670°C |      |
| 2004B   | Cu <sub>80</sub> Sn <sub>20</sub>                                       | 950°C |      |

(日本非晶質金属のパンフレットより) (21)

Key:

1. Amorphous alloys: magnetic materials
2. Brand
3. Composition (atom percent)
4. Major applications
5. Pulse transformer, sensor, power transformer
6. Power distribution transformer, choke coil, power transformer
7. Power source transformer for aircraft, pulse transformer, sensor
8. SMPS transformer, signal transformer
9. Small-sized signal transformer, magnetic shield

[Key continued on following page]

10. SMPS transformer, signal transformer
11. Magnetic head, sensor
12. Amorphous alloys Ni-base grazed foil
13. Brand
14. Official composition (wt percent)
15. Corresponding AWS
16. Grazing temperature (°C)
17. Amorphous alloys Cu-base grazed foil
18. Brand
19. Official composition (wt percent)
20. Grazing temperature
21. (Source: brochure of Japanese Amorphous Metals)

Toshiba, together with four Mitsui group companies, Mitsui Petrochemical Industries, Ltd.; Mitsui Shipbuilding & Engineering Co., Ltd.; Japan Steel Works, Ltd.; and Mitsui & Co., Ltd., accepted the patent and established Japan Amorphous Metals, a joint venture entity with Allied Corp., to purchase Allied's products.

Conversely, TDK will purchase the license from Allied Corp. and start production.

While many other manufactures have not decided how to proceed, it seems that some of them may take a chance and develop materials not covered by Allied's basic composition patent.

### 3-3 Shape Memory Alloys

#### 1) What is a shape memory alloy?

Shape memory alloy (SMA) refers to alloys with the following property: "If the alloy, molded into a certain shape, is heated to a high temperature, it memorizes the shape. Even if the shape is changed after the alloy is cooled to normal temperature, it resumes the original shape by being warmed." (T. Matsuda, et al., "Common Sense on the Latest Scientific Technology." TOKYO KEIZAI SHINBUN)

The presence of alloys with this intriguing property seems to have been known since about 1938. Full-fledged knowledge, however, started with the 1962 discovery, at the U.S. Naval Weapons Research Laboratory, that the nickel/titanium alloy (50:50) (later named "nitinole alloy") has a shape memory property.

The author will not elaborate on the shape memory theory, but only describe it as a type of "martensite transformation," a phenomenon particular to metals.

The martensite transformation, conventionally considered inherent to steel, has been found to occur in alloys as well. Research and development for shape memory alloys has progressed rapidly.

At least 20 types of shape memory alloys have been developed to date. Representative alloys are shown in Table 7.

Among the list in Table 7, commercialized alloys are Nitinole (TiNi alloy), Betailloy (Cu-Zn-Al) Cu-Al-Be alloys, etc.

Table 7. Alloys with Perfect Shape Memory Effect

表 7 完全な形状記憶効果を示合金名

| 合 金<br>(1)                    | 組 成<br>(2)           | Ms温度<br>(3) | As と Ms<br>の差(°C)<br>(4) |
|-------------------------------|----------------------|-------------|--------------------------|
| Ag-Cd                         | 44~49原子% Cd (5)      | -190~-50°C  | ~15                      |
| Au-Cd                         | 46.5~50原子% Cd (6)    | 30~100°C    | ~15                      |
| Cu-Al-Ni                      | 14~14.5重量% Al (7)    | 140~100°C   |                          |
|                               | 3~4.5重量% Ni (8)      | 190~40°C    | ~35                      |
| Cu-Au-Zn                      | 23~28原子% Au (9)      |             | ~6                       |
|                               | 45~47原子% Zn (10)     | 120~30°C    |                          |
| Cu-Sn                         | ~15原子% Sn (11)       | -180~-10°C  | ~10                      |
| Cu-Zn                         | 38.5~41.5重量% Zn (12) | -180~100°C  |                          |
| Cu-Zn-X<br>(X=Si, Sn, Al, Ga) | 数重量% X (13)          | 60~100°C    | ~10                      |
| In-Tl                         | 18~23原子% Tl (14)     | -180~100°C  | ~4                       |
| Ni-Al                         | 36~38原子% Al (15)     | -50~100°C   | ~10                      |
| Ti-Ni                         | 49~51原子% Ni (16)     | ~-130°C     | ~30                      |
| Fe-Pt                         | ~25原子% Pt (17)       | ~-100°C     | ~4                       |
| Fe-Pd                         | ~30原子% Pd (18)       | -250~180°C  |                          |
| Mn-Cu                         | 5~35原子% Cu (19)      |             | ~25                      |

(注) Ms 温度: アルテンサイト変態温度, As: 逆変態温度

(20) (「MOL」昭和60年5月号別冊, オーム社, 堂山, 山本編「新素材」培風館等を参照)

Key:

- |                                      |                                                                                                              |
|--------------------------------------|--------------------------------------------------------------------------------------------------------------|
| 1. Alloys                            | 15. 36-38 Atom% Al                                                                                           |
| 2. Composition                       | 16. 48-51 Atom% Ni                                                                                           |
| 3. Ms temperature                    | 17. -25 Atom% Pt                                                                                             |
| 4. Difference between As and Ms [°C] | 18. -30 Atom% Pd                                                                                             |
| 5. 44-49 Atom% Cd                    | 19. 5-35 Atom% Cu                                                                                            |
| 6. 46.6-50 Atom% Cd                  | 20. (Note)                                                                                                   |
| 7. 14-14.5 wt% Al                    | Ms temperature: Martensite transformation temperature                                                        |
| 8. 3-4.5 wt% Ni                      | As temperature: Reverse transformation temperature                                                           |
| 9. 23-28 Atom% Au                    | (MOL special issue May 85, Ohmu Co. Referred to "New Materials" edited by Doyama/Yamamoto, Baifukan, et al.) |
| 10. 45-47 Atom% Zn                   |                                                                                                              |
| 11. -15 Atom% Sn                     |                                                                                                              |
| 12. 38.5-41.5 wt% Zn                 |                                                                                                              |
| 13. several wt% X                    |                                                                                                              |
| 14. 18-23 Atom% Tl                   |                                                                                                              |

2) Development and Application of Shape Memory Alloys

Shape memory alloys are divided into two groups by their deformation property-one-way or two-way types. The former resumes its original shape when heated

after deformed at low temperature, but does not take the low temperature form again even if cooled to low temperature after heating. The latter memorizes both low temperature and high temperature forms, and thus the shape change is reversible.

Commercialization started with the one-way group.

The first application was to pipe joints. In the United States, more than 100,000 of them are said to be used in hydraulic piping for F-14 fighters, with no problems reported.

Other applications of one-way shape memory alloys include parabolic antennae to be installed on the moon's surface, antennae for artificial satellites, and civil uses such as electric connectors, IC package sealings, and clamps of various types. Studies are also underway for medical uses in dental implant material and scoliosis.

Commercialization of two-way shape memory alloys is lagging behind largely because of the difficulty in designing dimension accuracy on the high and low temperature sides. However, their application range is expected to be greater than for one-way alloys.

Possible fields of application are shown in Table 8.

In any event, the shape memory alloy is now entering an era when development of better materials, as well as exploration for prospective markets, is being aggressively pursued. This is one of the new metals whose future seems promising.

As to Japanese manufacturers of shape memory alloys, six companies - Furukawa Electric, an early developer of NiTi alloy and spearhead of the group, Tohoku Metal, Sumitomo Special Metals, Sumitomo Metal (which marketed Cu alloy - Memorion 100), Dowa Mining Co., Ltd., and Daido Special Metals, Co., Ltd., organized a research association to work positively on the subject. Other copper and titanium alloy manufacturers conducting their own development include Kobe Steel, Sumitomo Electric, Hitachi Metals, and Sumitomo Metal Mining.

### 3-4 Superplastic Alloys

#### 1) What are superplastic alloys?

Superplastic alloy refers to an alloy which stretches like candy when pulled out under certain conditions.

Superplasticity comes in two types: one occurs when microcrystals are deformed at a certain temperature (normally 800-900°C), the other relates to the deformation caused by heating across the transformation point. For industrial purposes, the former is utilized more frequently.

Table 8.

| Fields                  | Products                                                                                                   |
|-------------------------|------------------------------------------------------------------------------------------------------------|
| Engine or Engine system | thermal engine, offset crank-type engine turbine-type engine, kick-type engine, stepping-type engine, etc. |
| Domestic appliance      | air conditioner (louver switch, etc.)<br>microwave oven (damper driver)                                    |
| Hothouse                | automatic door/window, automatic drying chamber, temperature switch                                        |
| Toys                    | new idea toys, sundries                                                                                    |
| Others                  | robots, chemical plants, etc.                                                                              |

(SISCO)

The microcrystal type superplastic alloy requires ultrafine crystal technology on the order of microns. This type of alloy is found in large numbers with respective metals. Tables 9 and 10 list some representative ones.

#### 1) Application of Superplastic Alloys

Application of superplastic alloys to aircraft parts molded machine parts, etc., has been moving forward, taking advantage of the alloy's ability to exhibit ductility under small stress, and of the ease of taking to forging dies. It is considered possible to use them widely in the future. Some specialists in this field predict that about 25 percent of the metal machining process will utilize the superplasticity phenomenon in the near future.

Table 9.

| (1)       | (2)              | 表9 主な鉄鋼系超塑性材料 |             |         |            | (5)  | (6)  |
|-----------|------------------|---------------|-------------|---------|------------|------|------|
| 名称        | 組成(wt%)          | (3)<br>温度(°C) | (4)<br>最高m値 | 最大伸び(%) | 備考         |      |      |
| (7) 共析鋼   | Fe-0.8C          | 704           | 0.35        | 100     | 共析         | (12) |      |
| (7) 共析鋼   | Fe-0.91C-0.45Mn  | 716           | 0.42        | 133     | 共析         |      |      |
| (8) 過共析鋼  | Fe-1.3~1.9C      | 600~800       | 0.52        | 750     |            |      |      |
| (9) 白鉄    | Fe-2.6C          | 600~800       | 0.5         | —       |            |      |      |
| (10) 合金鋼  | Fe-0.42C-1.9Mn   | 727           | 0.5         | 460     | AISI 1340  |      |      |
| 合金鋼       | Fe-1.5Mn-0.8P    | 800~900       | 0.52        | 400     |            |      |      |
| 合金鋼       | Fe-1.5Ni-1.0P    | 800~900       | 0.52        | 400     |            |      |      |
| (11) 高合金鋼 | Fe-5Cr           | 850           | 0.28        | 152     |            |      |      |
| IN 744    | Fe-26Cr-6.5Ni    | 870~980       | 0.5         | 200~600 | Uniloy 326 |      |      |
| (11) 高合金鋼 | Fe-4Ni-4Mo-1.6Ti | 900           | 0.58        | 820     |            |      |      |
| Fe-Cu     | Fe-50Cu          | 800           | 0.32        | 300     | 粉末焼結材      | (13) | (14) |

(通産省機械技術研究所、大内清行のデータによる)

[Key on following page]

Key:

- |                          |                                    |
|--------------------------|------------------------------------|
| 1. Name                  | 9. White iron                      |
| 2. Composition (wt %)    | 10. Alloy steel                    |
| 3. Temperature (°C)      | 11. High alloy steel               |
| 4. Maximum m Value       | 12. Eutectic                       |
| 5. Maximum extension (%) | 13. Sintered powder material       |
| 6. Remarks               | 14. (Source: data by K. Ouchi,     |
| 7. Eutectoid steel       | Mechanical Engineering Laboratory, |
| 9. Hyper-eutectoid steel | MITI)                              |

Table 10. Major Non-iron Superplastic Materials

| 表10 主な非鉄系超塑性材料 |      |             |                               |           |         |          |              |
|----------------|------|-------------|-------------------------------|-----------|---------|----------|--------------|
| (1)            | (2)  | (3)         | (4)                           | (5)       | (6)     | (7)      |              |
|                | 合金系  | 名 称         | 組 成 (wt%)                     | 温度 (°C)   | 最高 m 値  | 最大伸び (%) | 備 考          |
| (8)            | Ag合金 | Ag-Cu       | Ag-28.1Cu                     | 675       | 0.53    | 500      | 共品 (13)      |
| (9)            | Al合金 | Al-Cu       | Al-17Cu                       | 400       | —       | 600      | 共品 (13)      |
|                |      | Al-Cu       | Al-33Cu                       | 440~520   | 0.8     | >500     |              |
|                |      | Al-Cu-Mg    | Al-33Cu-7Mg                   | 420~480   | 0.72    | >600     |              |
|                |      | Al-Cu-Mg    | Al-25Cu-11Mg                  | 420~480   | 0.69    | >600     |              |
|                |      | Al-Cu-Si    | Al-25.2Cu-5.2Si               | 500       | 0.43    | 1,310    |              |
|                |      | Supral 150  | Al-6Cu-0.5Zr                  | 350~475   | 0.5     | >1,000   |              |
|                |      | Al-Mg-Zr    | Al-6Mg-0.4Zr                  | 400~520   | 0.6     | 890      |              |
|                |      | Al-Si       | Al-11.7Si                     | 450~550   | 0.28    | 480      |              |
|                |      | BA708       | Al-6Zn-3Mg                    | 320~400   | 0.35    | 400      |              |
|                |      | AA7075      | Al-5.6Zn-2.5Mg-1.6Cu-0.3Cr    | 350~475   | 0.41    | 190      |              |
| (10)           | Ni合金 | Al-Zn-Mg-Zr | Al-10.7Zn-0.9Mg-0.4Zr         | 550       | 0.9     | 1,550    | 粉末焼結押出材 (14) |
|                |      | Al-Zn-Zr-Sn | Al-5~10Zn-0.5Zr-0.05Sn        | 550       | 0.7     | 800      |              |
|                |      | Ni          | Pure                          | 820       | —       | 225      |              |
|                |      | IN100       | Ni-10Cr-15Co-4.5Ti-5.5Al-3Mo  | 927~1,093 | 0.5     | 1,300    |              |
| (11)           | Pb合金 | Ni-Cr-Fe    | Ni-39Cr-10Fe-1.75Ti-1Al       | 810~980   | 0.5     | ~1,000   | 共品 (13)      |
|                |      | Ni-Fe-Cr-Ti | Ni-26.2Fe-34.9Cr-0.58Ti       | 795~855   | 0.5     | >1,000   |              |
|                |      | Pb-Cd       | Pb-5Cd                        | 50        | 0.35    | —        |              |
|                |      | Pd-Cd       | Pb-17.6Cd                     | 100       | 0.5~0.6 | >350     |              |
| (12)           | Ti合金 | Pb-Sn       | Pb-19Sn                       | 20        | 0.5     | >500     | 共品 (13)      |
|                |      | Pb-Th       | Pb-7.9Th                      | —         | 0.5     | 372      |              |
|                |      | IMI317      | Ti-5Al-2.5Sn                  | 900~1,100 | 0.72    | 450      |              |
|                |      | IMI318      | Ti-6Al-4V                     | 800~1,000 | 0.85    | 1,000    |              |
|                |      | Ti-Al       | Ti-4Al-2.5O                   | 950~1,050 | 0.6     | —        |              |
|                |      | Ti-Cr-V-Al  | Ti-13Cr-11V-3Al-0.15O         | 900       | ~1.0    | 150      |              |
|                |      | Ti-Mn       | Ti-8Mn-0.14O                  | 900       | ~1.0    | 150      |              |
|                |      | Ti-Mo       | Ti-15Mo-0.18O                 | 920       | ~1.0    | 450      |              |
|                |      | IMI679      | Ti-11Sn-2.25Al-1Mo-5Zr-0.25Si | 800       | —       | 500      |              |
|                |      | IMI700      | Ti-6Al-5Zr-4Mo-1Cu-0.25Si     | 800       | —       | 300      |              |

(15) (通産省機械技術研究所、大内清行のデータによる)

Key:

- |                                                                         |                          |                                         |
|-------------------------------------------------------------------------|--------------------------|-----------------------------------------|
| 1. Alloy group                                                          | 6. Maximum extension (%) | 11. Pb alloys                           |
| 2. Name                                                                 | 7. Remarks               | 12. Ti alloys                           |
| 3. Composition (wt%)                                                    | 8. Ag alloys             | 13. Eutectic                            |
| 4. Temperature (°C)                                                     | 9. Al alloys             | 14. Sintered powder extrusion materials |
| 5. Maximum m value                                                      | 10. Ni alloys            |                                         |
| 15. (Source: data by K. Ouchi, Mechanical Engineering Laboratory, MITI) |                          |                                         |

### 3-5 Vibration-Proof Alloys

#### 1) What is a vibration-proof alloy?

Metal which does not make a sound when it is hit is a vibration-proof alloy.

In general, the damping capacity of metals against vibration is small and their deficiency is to resound in high metallic tones when struck. Noise pollution, which has recently become a major social problem following the population concentration in cities, is partly attributable to this metallic sound.

Need for vibration-proof alloys has been growing.

The vibration sound of metals and other materials can be prevented by: (1) a vibration-proof system (to absorb vibrations by providing an outside damper system such as an oil or air damper), (2) structural improvements (to absorb vibrations by sandwiching visco-elastic high polymer materials between metals) and (3) improvements in the material itself.

The effect of methods (1) and (2) is to soften the metallic sound generated, and their possible application is limited to a certain temperature range. Because of such shortcomings, improvement of the material itself is recently receiving more attention.

Examples of vibration-proof alloys developed so far are shown in Table 11.

#### (1) Compound Type

This is made up of the mixture of two phases, such as eutectoid and eutectic, and is represented by Al-Zn alloys, etc.

#### (2) Ferromagnetism Type

The major materials in this category are soft magnetism materials, which use a phenomenon called magnetic/mechanical static hysteresis. The effect can be obtained even under temperatures as high as 700°C.

A representative is Silentalloy (Fe-Cr-Al alloy), developed and marketed by Toshiba, and Tranqualloy (Fe-Cr-Al-Mn alloy), by Nippon Kokan.

#### (3) Dislocation Type

Mainly hexagonal metals are used in this type. Mo-Zr alloy and Mg-MgNi quasi-eutectic alloys have been developed.

#### (4) Twin Type

This category includes thermally elastic martensite metals such as Ni-Cu alloy, Cu-Al-Ni alloy and TiNi alloy. There are still unresolved problems with this type.

2) Applications of vibration-proof alloys, shown in Table 12, have just started in very specialized fields and have not reached full-scale dissemination. Future promising fields of application are shown in Table 13.

Table 11. Classification of Vibration-proof Alloys

(2) 表11 防振合金の分類

| (1) 分類                                             | (3) 例                                                           |                                                                                                                                                                               | (6) 製造販売会社                                                                                                                                        |
|----------------------------------------------------|-----------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|
|                                                    | (4) 合金名                                                         | (5) 実用合金                                                                                                                                                                      |                                                                                                                                                   |
| (7) 複合型<br>(応力緩和型)                                 | Fe-C-Si<br>Al-Zn*                                               | 片状黒鉛鋳鉄 (11)<br>SPZ(Super Plastic Zinc の略,<br>Zn-22Al)                                                                                                                         | (一般構造用材料) (16)<br>日本では三井金属鉱業 (17)                                                                                                                 |
| (8) 強磁性型<br>(ヒステリシス型)                              | Fe, Ni<br>Fe-Cr<br>Fe-Cr-Al<br>Fe-Cr-Al-Mn<br>Fe-Cr-Mo<br>Co-Ni | TDニッケル (12)<br>12%Cr鋼 (13)<br>サイレントロイ (Silentalloy, Fe-12Cr-3Al)<br>トランカロイ (Tranqualloy, Fe-12Cr-1.36Al-0.59Mn)<br>ゲンダロイ (Gentalloy, Fe-0.1~5Mo)<br>NIVCO-10(Co-22Ni-2Ti-1Zr) | (実用耐熱合金) (18)<br>(フェライト系ステンレス鋼のベース鋼) (19)<br>日本, 東芝 (20)<br>日本, 日本鋼管 (21)<br>日本, 財団法人電気磁気材料研究所, 特許出願公告 昭56-26709<br>(実用耐熱合金で, タービン翼用材料として使用されている) |
| (9) 転位型<br>(ヒステリシス型)                               | Mg, Mg-Zr<br>Mg-Mg <sub>2</sub> Ni                              | KIXI合金(Mg-0.6Zr) (14)                                                                                                                                                         | 米国, Dow Chemical社 (23)                                                                                                                            |
| (10) 双晶型<br>ヒステリシス型<br>.....*印<br>応力緩和型<br>...それ以外 | Mn-Cu<br>Mn-Cu-Al<br>Cu-Al-Ni*<br>Cu-Zk-Al*<br>NiTi*            | ソノストーン (Sonostone, Mn-37Cu-4.25Al-3Fe-1.5Ni)<br>インクラミュート<br>(Incramate I, Cu-40Mn-2Al)<br>(Incramate II, Cu-40Mn-2Al-2Sn)<br>ニチノール (Ni-50Ti) (15)                             | 米国, Manganese Marine社<br>米国, International Copper Research Association社<br>---<br>---<br>日本では古河鉱業 (24)                                            |

(22)

(25)

\*印: 形状記憶効果 (超弾性) 合金でもある      \*\*印: 超塑性合金でもある  
(鳥阪泰憲「防振合金」日工マテリアルVOL.1 12月号)

Key:

- |                                           |                                                                 |
|-------------------------------------------|-----------------------------------------------------------------|
| 1. Classification                         | 12. TD nickel                                                   |
| 2. Name                                   | 13. 12% Cr steel                                                |
| 3. Examples                               | 14. KIXI alloy                                                  |
| 4. Alloy name                             | 15. Nitinole                                                    |
| 5. Practical alloy                        | 16. (General building materials)                                |
| 6. Manufacturer/marketer                  | 17. In Japan, Mitsui Mining and Smelting Co., Ltd.              |
| 7. Compound type (stress relaxation type) | 18. (Practical heat-resistant alloys)                           |
| 8. High magnetism type (hysteresis type)  | 19. (Base steel for ferrite stainless steel)                    |
| 9. Dislocation (hysteresis type)          | 20. In Japan, Toshiba, Co., Ltd.                                |
| 10. Twin type                             | 21. In Japan, Nippon Kokan Kabushiki Kaisha                     |
| Hysteresis type                           | 22. In Japan, Electric Magnetic Material Research Foundation.   |
| .....* mark                               | Patent application published 1981-26709                         |
| Stress relaxation type                    | (practical heat-resistant alloy used as turbine blade material) |
| ... others                                |                                                                 |
| 11. graphite cast iron flake              |                                                                 |

[Key continued on following page]

23. In the United States  
 24. In Japan, Furukawa Mining Co., Ltd.  
 25. \*mark: Shape memory effect (super elasticity) alloy  
 \*\*mark: Superplastic alloy  
 (Y. Torisaka "Non-Vibration Alloys"  
 NIKKO MATERIAL Vol 1 Dec)

Table 12. Application of Non-Vibration Alloys to Noise Control

| Alloy Name                     | Applications                                                                                                                                  | Effects                                                                                                                |
|--------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------|
| Sonostone                      | Submarine screw<br><br>Chain conveyer<br>High speed tape puncher<br>Mechanical filter frame<br>Rock drill<br>Ball Bearing<br>Soundproof wheel | Actually used for more than 10 years<br><br>92 phone→87 phone<br>-14 db<br>111 db→98 db<br><br>-6 db (hammering sound) |
| Ingramute                      | Hot cutlery hammer<br>Disc saw<br>Disposal                                                                                                    | -13~-30 db                                                                                                             |
| Silentalloy                    | DC solenoid plunger<br>Railroad repair machine<br>Large power direct current shutter<br>Piston head<br>Door, shutter, office equipment        | -4 db<br><br>-2~-4 db                                                                                                  |
| Graphite cast iron rolled ball | Disc saw                                                                                                                                      | -10 db                                                                                                                 |
| Fe-Cr-Al alloy                 | M113 type tank                                                                                                                                | -10 db at 50 miles/hour                                                                                                |

(K. Sugimoto "Non-Vibration Alloy: Metal Material in Extreme Conditions"  
 Industrial Research Committee)

Table 13.

| Field                             | Planned Applications                                                                                               |
|-----------------------------------|--------------------------------------------------------------------------------------------------------------------|
| Space/Aviation                    | Control panel for rocket, missile, jet; gyrocompass, engine cover, turbine blade                                   |
| Automobile                        | Car body, disc break, parts surrounding engine, emission, air cleaner                                              |
| Construction<br>Civil engineering | Bridge, rock drill, sound-proof material for steel staircase work                                                  |
| Machinery                         | Press, chain conveyer, gear                                                                                        |
| Railroad                          | Wheel, rail                                                                                                        |
| Ship                              | Engine parts, screw                                                                                                |
| Domestic appliances               | Air conditioner, washing machine, electricity breaker, transformer sound-proof cover, speaker parts, turbine parts |

(SISCO)

### 3-6 Hydrogen Occlusion Alloys

Hydrogen occlusion alloys refer to those with the function of absorbing/retaining hydrogen in the form of metal hydride and releasing it whenever it is needed.

The first metal with this characteristic was found by the Philips Company in the Netherlands, from which dates the attention presently given to this type of alloy.

This article will not discuss its theory. Alloys presently reported among the hydrogen occlusion type are shown in Table 14.

As to the application, the primary objective is to store hydrogen to meet the high expectations given to hydrogen as a clean energy source for various purposes. Specifically these alloys are used for the hydrogen automobile, heat exchanger, cooler/freezer, heat pipe, etc.

Manufacturers of hydrogen occlusion alloys include Giken Kagaku, Mitsubishi Corporation, Santoku Kinzoku Kogyo and Mitsubishi Steel.

Companies shown in Table 15 are involved in developing applications.

Table 14. Types and Characteristics of Hydrogen Retention (Occlusion) Alloy

| Alloy Name | Occlusion/<br>Release<br>Capability | Hydrogen<br>Release<br>Condition | Cost          | Others                    |
|------------|-------------------------------------|----------------------------------|---------------|---------------------------|
| Fe-Ti      | good                                | excellent                        | low           | lowest cost               |
| Ti-Mn      | satisfactory                        | good                             | low           | for aluminum<br>container |
| La-Ni      | "                                   | excellent                        | high          | best quality<br>materials |
| La-Ce-Ni   | "                                   | good                             | slightly high |                           |
| Mg-Ni      | "                                   | satisfactory                     | low           | for automobile            |

The evaluation is in the order of excellent good satisfactory. (SISCO)

Table 15. Hydrogen Retention (Occlusion) Alloy Application Development

|               | Companies                          |                                                                                                                                                                                                     |
|---------------|------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Japan         | Showa Denko K.K.                   | °concluded contract with U.S. MPD for marketing both alloys and related equipment, and for joint development                                                                                        |
|               | Japan Metals & Chemicals Co., Ltd. | °developed Japan's first hydrogen retention cylinder using a hydrogen retention alloy                                                                                                               |
|               | Chuo Electric Industry             | °mass-produced 5 tons/month of hydrogen retention alloy First time in Japan                                                                                                                         |
|               | Iwatani & Co., Ltd.                | °developed jointly with U.S. MPD a "metal hydrogen compound container" for commercial use                                                                                                           |
|               | Kyodo Sanso [Oxygen]               | °produced trial model of hydrogen sedan to achieve 80km/hr                                                                                                                                          |
| United States | MPD                                | °maintains world's largest share, at least 50%                                                                                                                                                      |
|               | Brookhaven National Laboratory     | °the authority on studies of hydrogen retention alloys and their applications; developed the technology to deposit excessive electricity generated during the night using hydrogen retention alloys |
| Europe        | Daimler-Benz                       | °developed hydrogen engine bus using hydrogen retention alloys                                                                                                                                      |

(MOL May 1985, special issue, Ohmu Co. "Net Material" edited by Doyama/Yamamoto, Baifukan)

#### 4. Market Trend of New Metal Materials

We have summarized representative new metals and their developmental status, as well as future prospects, for the materials and their application. For any of these new materials, excluding a few cases, development of the market is just getting started. It is impossible to determine the market scale at this moment, but the future market is expected to be very large.

According to data of the Industrial Structure Council, an advisory organ to MITI, a new metals market in the year 2000 of ¥1.5 trillion is predicted. This is comparable to the fine ceramics market.

20126/12712

CSO: 4106/5017

## NEW MATERIALS

### PRESENT STATUS AND PROSPECTS OF FINE CERAMICS

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[Article by Eiji Kamijo, assistant manager, Itami Reserach Department, R&D Division, Sumitomo Electric Industries, Ltd.: "Trends of Fine Ceramics Development"]

#### [Excerpts] 1. Preface

The ceramic industry is one of the oldest industries. It began with the history of mankind, and has largely outgrown its former self in the current age of new ceramics. The ceramic industry is a pottery business; it makes products by heating natural mineral raw materials to a high temperature in a kiln or oven. It was 1887 when "yogyo" in Japanese, was translated as "ceramics." The word is known to have originated from a Greek term "keramos" (earthenware), and its products are rperesented by porcelain, brick, glass, and cement.

With the industrial level sharply rising in recent years, the demand for basic materials to support new functions and characteristics has increased as a matter of course. The dependence on the existing natural mineral raw materials could not keep pace with such demands, so the ceramic industry managed to meet the demand by applying a highly controlled process using refined raw materials of high purity. As a result, non-oxide base ceramics such as a nitrogeneous compound, carbide and boride, which do not occur in nature, have come into the picture as new substances in addition to the existing oxide base ceramics.

The existing ceramics using natural mineral raw materials, including the above-mentioned porcelain, are called "classic ceramics" or "traditional ceramics." The ceramics using refined artificial raw materials, whose characteristics are highly controlled, are called "new ceramics" or "fine ceramics." The terms of new ceramics and fine ceramics are Japan's own, whereas in foreign countries, including the United States, they are called "high technology ceramics," "high performance ceramics" or "advanced ceramics" from the standpoint that they are important basic materials for sustaining advanced technologies.

The efforts to apply the unlimited potential of fine ceramics as new materials which can contribute to technological innovation in the next generation are presently very active, so much so that the efforts are felt to be somewhat overheated, like a fine ceramics fever.

Fine ceramics are, however, still in their infancy as materials and have many aspects which have not yet been technologically established. Thus their future prospects are not necessarily defined. Conducting research and development following the beaten track over a long period of time and the consequent consolidation of the fundamentals of the ceramic industry are considered necessary in order to take long strides in the future.

## 2. Why Fine Ceramics Came on the Scene at This Time

Fine ceramics are not only important materials playing a role in dealing with the issues of energy and resources. They are expected to become new materials contributing to the development and progress of the electronics industry, which helps pave the way for oceanic development, the aerospace industry and an information society, all of which fall under the new demand areas. Their market size is estimated in Figure 1. The use of fine ceramics as basic formative materials and mechanical parts, not as mere basic materials, will result in the development of various machines equipped with new functions. This fine ceramics are viewed to have far-reaching technological effects and fill great social needs in the following areas.

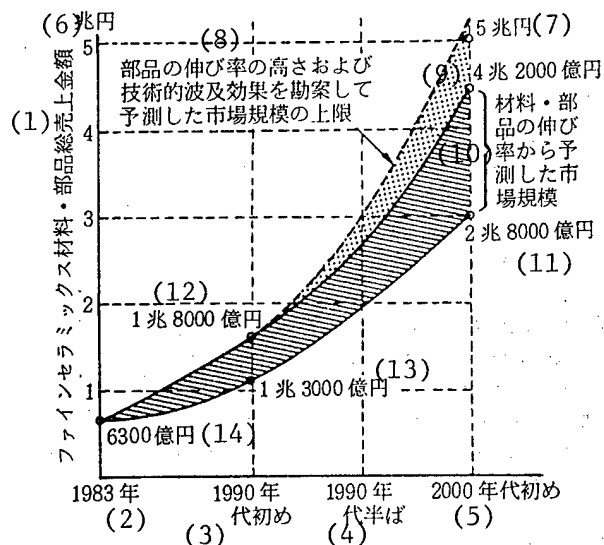
### 2.1. Damage-Resistant Materials Required for Advanced Industries

Fine ceramics are important materials able to meet strong demands from advanced industries requiring new materials capable of withstanding the severe environmental conditions under existing materials can not hold out.

Figure 1. Estimate of Fine Ceramics  
Market Size (Module base)  
(MITI survey)

Key:

1. Total sales value of fine ceramic materials and parts
2. 1983
3. Early in 1990's
4. Mid-1990's
5. Early in 2000
6. In trillions of yen
7. Trillion yen
8. Estimated ceiling of market size taking into account the growth rate of parts and far-reaching technological effects
9. 4.2 trillion yen
10. Market size estimated from growth rates of materials and parts
11. 2.8 trillion yen
12. 1.8 trillion yen
13. 1.3 trillion yen
14. 630 billion yen



## 2.2. Activation of Existing Industries

Fine ceramics are expected to contribute to diversifying and activating the existing material industries such as ceramics, chemistry, steel and iron, and nonferrous metals. Their effects are also expected to make devices, machines and various consumer goods smaller and lighter, their useful life younger, and to up grade their functions.

## 2.3. Saving of Energy and Rare Metal Resources

The United States and West Germany are wrestling with the task of applying fine ceramics to a heat engine and heat exchanger. This is a national project for both countries. Fine ceramics are considered to permit operation at a high temperature and the utilization of intense heat. In so doing, they can greatly enhance energy efficiency, eventually resulting in energy-saving.

As a heat resistant alloy rare metal resources such as nickel, chrome, cobalt and molybdenum are used in quantities at present. However, fine ceramics such as silicon nitride ( $\text{Si}_3\text{N}_4$ ) and silicon carbide ( $\text{SiC}$ ) can serve as their substitutes.

This seems to be due to the recognized fact that the development of new basic materials will have a major impact on the economy and that it will contribute significantly to the strengthening of international competitiveness.

Social needs are on the increase. The results of basic research on fine ceramics ( $\text{Si}_3\text{N}_4$ ,  $\text{SiC}$ ,  $\text{ZrO}_2$ , etc.) which has steadily been carried out since early in the 1950's in the United Kingdom, the United States and Japan, became technological seeds and are gradually blooming. These needs and seeds started to combine early in 1980's to produce the present fine ceramics fever.

## 3. Functions and Applications of Fine Ceramics

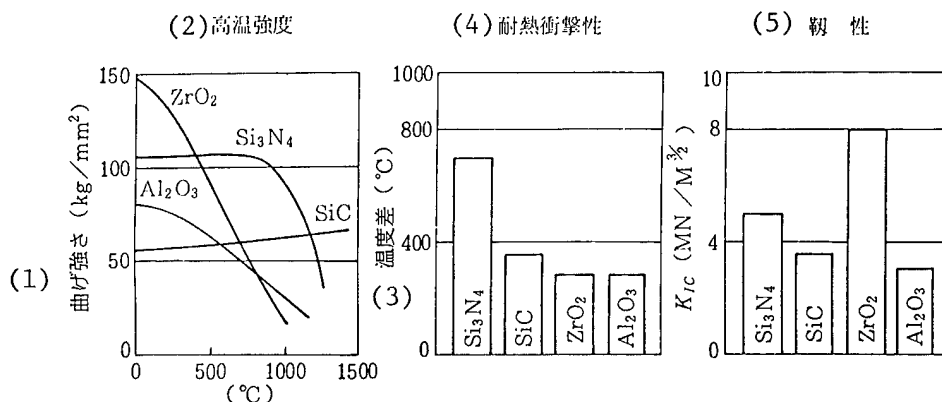
Although there are various ways to classify the kinds and usages of fine ceramics, this article largely divides them into two categories as follows:

- (1) Functional ceramics
- (2) Engineering ceramics

The functional ceramics, which utilize physical, chemical and electromagnetic functions inherent in ceramics, have developed in response to advances in the electronic industry. The engineering ceramics are intended to take advantage of the mechanical, thermal and chemical characteristics inherent in ceramics such as strength and hardness and to apply these to machine components as wearproof, anticorrosive and heat-resistant materials.

A very promising application area for the utilization fine ceramics is found in the component parts of machines. The materials primarily used there are silicon nitride ( $\text{Si}_3\text{N}_4$ ), silicon carbide ( $\text{SiC}$ ), zirconium oxide ( $\text{ZrO}_2$ ) and aluminum oxide ( $\text{Al}_2\text{O}_3$ ). The characteristics of these materials are shown in Figure 2.

Figure 2. Material Characteristics of Engineering Fine Ceramics



Key:

- |                                      |                              |
|--------------------------------------|------------------------------|
| 1. Bending Strength                  | 3. Difference of temperature |
| 2. Strength against high temperature | 4. Thermal impact-resistance |
|                                      | 5. Tenacity                  |

Each kind of material has its own characteristics and the applications of such characteristics are being examined. With respect to  $ZrO_2$ , the application of its bonding to cutlery used at normal room temperature surpassed any other application. As for  $Si_3N_4$ , the application of its balanced characteristic in a temperature range of below  $1,000^\circ C$  to auto engine materials is now under study. The application of  $SiC$ , which is superior in a high temperature range of more than  $1,000^\circ C$ , is being examined with regard to a gas turbine engine. Such information is consolidated in Table 1.

The present status, future prospects and tasks of fine ceramics will be described below, centering on engineering ceramics.

#### 4. Present Status of Engineering Ceramics

There were unsuccessful attempts in the past to use ceramics as machine parts resistant to intense heat, utilizing their superior mechanical and thermal characteristics.

The research and development of  $Si_3N_4$  and  $SiC$  started in the late 1950's, with the materials being regarded as useful because of their high strength and resistance to high temperatures.

In 1971 the United States took on as a national project the research designed to replace with ceramics the various heat-resisting materials used in a gas turbine whose inlet temperature is  $1,371^\circ C$ . Since that time, research work of this kind has made rapid progress. As a result, the application of ceramics to gas turbines, auto engines, parts of various industrial machines, golf club faces, and scissors has been planned. The ceramic applications now under examination as engineering materials are shown in Table 2.

Table 1. Characteristics of Representative  
Fine Ceramics

| Base                    | General Characteristics                                            | Materials                                 | Characteristics of Physical Properties                                                                                              | Applications as Engineering Materials                              | Remarks                                                                                                                                                                                                                                                                                                             |
|-------------------------|--------------------------------------------------------------------|-------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Oxide Base Ceramics     | 1. Natural raw materials are mostly used.                          | Alumina (Al <sub>2</sub> O <sub>3</sub> ) | Hard, wearproof, insulating, anticorrosive                                                                                          | Cutting tools, pump parts, thread guides                           | * Leader of ceramic materials at present.                                                                                                                                                                                                                                                                           |
|                         | 2. It is comparatively easy to sinter.                             |                                           |                                                                                                                                     |                                                                    | * To improve characteristics of raw powder the upgrading of purity and fineness are required.                                                                                                                                                                                                                       |
|                         | 3. Thermal and electric conductivity are minor.                    | Zirconia (ZrO <sub>2</sub> )              | Oxygen ion conductive, adiabatic (High strength, high tenacity) (Thermal impact-resistant) (Wearproof, low coefficient of abrasion) | Adiabatic and insulating materials<br>Cutlery<br>Rubbing materials | * Pure zirconia is difficult to sinter because of phase modification. Additives of CaO, MgO and Y <sub>2</sub> O <sub>3</sub> stabilize.                                                                                                                                                                            |
|                         | 4. Highly anti-corrosive                                           |                                           |                                                                                                                                     |                                                                    | * Partly stabilized zirconia is spotlighted as high strength ceramics.                                                                                                                                                                                                                                              |
| Non-Oxide Base Ceramics | 1. They do not occur in nature (synthetic raw materials are used.) | SiC                                       | Hard, wearproof<br>Heat-resistant<br>Electric conductivity<br>Thermal conductivity                                                  | Mechanical seal<br>Setters<br>Reactor core tubes                   | * The discovery of auxiliary sintering agents B and C is the key to the future development.                                                                                                                                                                                                                         |
|                         | 2. Sintering is difficult.                                         |                                           |                                                                                                                                     |                                                                    | * They are much expected as heat-resisting materials.                                                                                                                                                                                                                                                               |
|                         | 3. They are generally hard and brittle.                            | Si <sub>3</sub> N <sub>4</sub>            | Hard<br>Heat-resistant<br>Thermal impact-resistant                                                                                  | Turbine blades<br>Bearings used under high temperature             | * They are much expected as heat-resistant materials.                                                                                                                                                                                                                                                               |
|                         | 4. Low specific gravity<br>5. Highly heat-resistant                |                                           |                                                                                                                                     |                                                                    | * The discovery of good sintering agents is expected like SiC (presently oxide compounds such as Al <sub>2</sub> O <sub>3</sub> , Y <sub>2</sub> O <sub>3</sub> and MgO are used.)<br>(Since WC, TiC and TiN are difficult to sinter, they are intended for composite materials using Ni and Co as bonding phases.) |

Table 2. Examples of Functions and Applications of Fine Ceramics

| Engineering Fine Ceramics | Mechanical Characteristics | Functions               | Materials                                                   | Examples                                        |
|---------------------------|----------------------------|-------------------------|-------------------------------------------------------------|-------------------------------------------------|
|                           |                            | Hardness                | Diamond, $B_4C$ , SiC, $Si_3N_4$ , TiC, TiN, $Al_2O_3$ , WC | Abrasives, grindstones<br>Cutting tools         |
|                           |                            | Strength                | $Al_2O_3$ , SiC, $Si_3N_4$<br>Zirconia                      | Parts for structural materials<br>Machine parts |
|                           |                            | Heat-resisting strength | $Si_3N_4$ , SiC                                             | Diesel engines<br>Gas turbine engines           |
|                           |                            | Anticorrosive           | $Al_2O_3$ , $ZrO_2$ , SiC                                   | Pumps, valves,<br>Chemical apparatuses          |
|                           |                            | Wearproof               | $B_4C$ , SiC, $Si_3N_4$                                     | A variety of rubbing parts                      |
|                           | Thermal Characteristics    | Heat-resistant          | $ThO_2$                                                     | Walls of high temperature furnaces              |
|                           |                            | Adiabatic               | $SiO_2$<br>$Al_2O_3$ fiber<br>$ZrO_2$                       | Insulating materials<br>Insulating engine parts |
|                           |                            | Heat conductive         | BeO, SiC                                                    | Heat exchangers                                 |

Behind the application of fine ceramics to heat engines, which has recently come into the limelight, there were meetings between "needs and seeds" as follows:

- 1) The fine ceramics provided with high thermal functions and resitive to severe stress conditions were demanded in the following areas:
  - (1) Energy saving through the development of a high efficiency engine and heat exchanger operable at a higher temperature;
  - (2) Resource conservation by substituting rare metals such as Ni, Cr, Co and Mo;
  - (3) Upgrading the required performance of fine ceramics such as anticorrosion, wearproof and long life under operation at a higher temperature.

2) Requirements in relation to the advancement of research and development of fine ceramics having high thermal functions:

(1) The development of process technology of covalent bond ceramics centering on  $\text{Si}_3\text{N}_4$  and  $\text{SiC}$ , and  $\text{ZrO}_2$  ceramics provided with high tenacity.

(2) The progress in the evaluation of characteristics and applied characteristics.

(3) The development and evolution of designing methods making the most of the characteristics of ceramics.

The effects of application of fine ceramics to heat engines are shown in Table 3.

The characteristics and applications of main engineering ceramics will be described as follows.

#### 4.1. $\text{Si}_3\text{N}_4$ Ceramics

$\text{Si}_3\text{N}_4$  and  $\text{SiC}$  are materials from which high strength can be expected because of their strong covalent bond. At the same time, the materials having such characteristics represent those difficult to sinter. In general, oxide additives such as  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  are used to promote the sintering of these materials.

Since a glass phase existing between particles of  $\text{Si}_3\text{N}_4$  softens at a high temperature, its strength reduces when applying this method. Therefore, researchers are actively attempting to improve the reduction of strength under high temperatures by applying the hot press and HIP methods using decreased amounts of oxide additives, and the gas pressure sintering method to sinter under high temperatures and high gas pressure, adding a substance of the high softening point.

$\text{Si}_3\text{N}_4$  is large in thermal conductivity when compared with other ceramics. It is small in the coefficient of thermal expansion and highly resistant to thermal impact. Moreover, it shows superior performance as a heat-resistant material under a temperature below 1,000–1,200°C, so it is expected to be used as the material for engines and as wearproof material.

#### 4.2. Sialon Ceramics

Sialon is constituted by replacing in part the Si and N of  $\text{Si}_3\text{N}_4$  with Al and O, i.e., it is an oxided and nitrogenous compound of Si and Al, and therefore called Sialon. It is regarded as promising as a material resistant to high temperatures and of high strength.

#### 4.3. $\text{SiC}$ Ceramics

A high density  $\text{SiC}$  sinter has been developed by adding a very small amount of auxiliary sintering agents B and C to  $\text{SiC}$ , and the results reported indicate that the more the temperature rises, the more the strength increases.

Table 3. Effects of Applications to Auto Parts

| Results Expected of Automobiles | Contents of Examination                                                                                                                                                                                                                                         | Ceramic Characteristics Utilized                                                                                                                         |
|---------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------|
| Improved fuel efficiency        | <ul style="list-style-type: none"> <li>* Improved combustion</li> <li>* Recycled exhausted energy (←raised exhaust gas temperature)</li> <li>* Reduced horse power loss (Reduced abrasion loss, no coolant, no lubricants)</li> <li>* Reduced weight</li> </ul> | Adiabatic efficiency<br>Heat-resistance, adiabatic efficiency<br>Abrasion, wear characteristics<br>Heat-resistance, adiabatic efficiency<br>Light weight |
| Upgraded performance            | <ul style="list-style-type: none"> <li>* Raised output by high temperature combustion</li> <li>* Upgraded turbo charger performance (Improved response, motion at higher temperature)</li> </ul>                                                                | Heat-resistance<br>Light weight, heat-resistance<br>Adiabatic efficiency                                                                                 |
| Reduced Noise                   | <ul style="list-style-type: none"> <li>* Improved combustion</li> <li>* Reduced clearance (Piston, moving valve system)</li> </ul>                                                                                                                              | Adiabatic efficiency<br>Low thermal expansion                                                                                                            |
| Improved durability             | <ul style="list-style-type: none"> <li>* Reduced wear troubles</li> <li>* Reduced corrosion troubles</li> </ul>                                                                                                                                                 | Abrasion, wear characteristics<br>Anticorrosion                                                                                                          |
| Purified exhaust gas            | <ul style="list-style-type: none"> <li>* Improved combustion</li> <li>* Diesel soot collection</li> </ul>                                                                                                                                                       | Adiabatic efficiency<br>Heat-resistance                                                                                                                  |
| Response to substitute fuels    | <ul style="list-style-type: none"> <li>* Response to cetan-reduced diesel fuel</li> </ul>                                                                                                                                                                       | Adiabatic efficiency                                                                                                                                     |
| Response to resources problem   | <ul style="list-style-type: none"> <li>* Substitutes for valuable metals</li> </ul>                                                                                                                                                                             | Heat-resistance, abrasion and wear characteristics                                                                                                       |
| Response to new power sources   | <ul style="list-style-type: none"> <li>* Higher efficiency of small gas turbines</li> </ul>                                                                                                                                                                     | Heat-resistance                                                                                                                                          |

Other than this, the development of a reaction SiC sinter and a SiC sinter, using oxidized additives such as  $\text{Al}_2\text{O}_3$ , and being carried out.

SiC is inferior to  $\text{Si}_3\text{N}_4$  in terms of the resistance to heat and impact because its hardness and coefficient of elasticity are high. It is nonetheless expected to be used as a material resistive to intensive scouring, as well as being wearproof and anticorrosive. In the meantime, its application in parts of a high temperature gas turbines, taking advantage of its resistance to high temperatures, is developing in foreign countries.

#### 4.4. $\text{ZrO}_2$ Ceramics

$\text{ZrO}_2$  develops the martensite modification at a temperature close to  $1,000^\circ\text{C}$ , resulting in volume changes and subsequent breakage. Thus, it is used by changing into a stable square crystal through the addition of crystal stabilizers such as  $\text{CaO}$ ,  $\text{MgO}$  and  $\text{Y}_2\text{O}_3$ .

Recently, a partly stabilized  $\text{ZrO}_2$  has been developed, which keeps in part a residual square crystal, an unstabilized phase, by controlling the quantity of stabilizers. A  $\text{ZrO}_2$  ceramic having largely upgraded characteristics specified below has been developed and is drawing public attention: the strength at the indoor temperature was raised to  $150\text{--}200 \text{ kg/mm}^2$  and the value of breaking tenacity ( $K_{Ic}$ ), which shows tenacity to  $10\text{--}15 \text{ MN/M}^{3/2}$ .

Since the partly stabilized  $\text{ZrO}_2$  is superior in terms of edging because of its strength at room temperature and its high tenacity, its application to cutlery is developing. However, there is the demand to make the crystal particles ultrafine.

$\text{ZrO}_2$  is low in thermal conductivity and has a coefficient of thermal expansion close to that of cast iron. Consequently, it is being attempted to apply it together with cast iron to heat insulating engine parts. Army trucks mounted with heat-insulated engines have been jointly developed by Cummins of the United States with the U.S. Army.

### 5. Themes of Technological Development

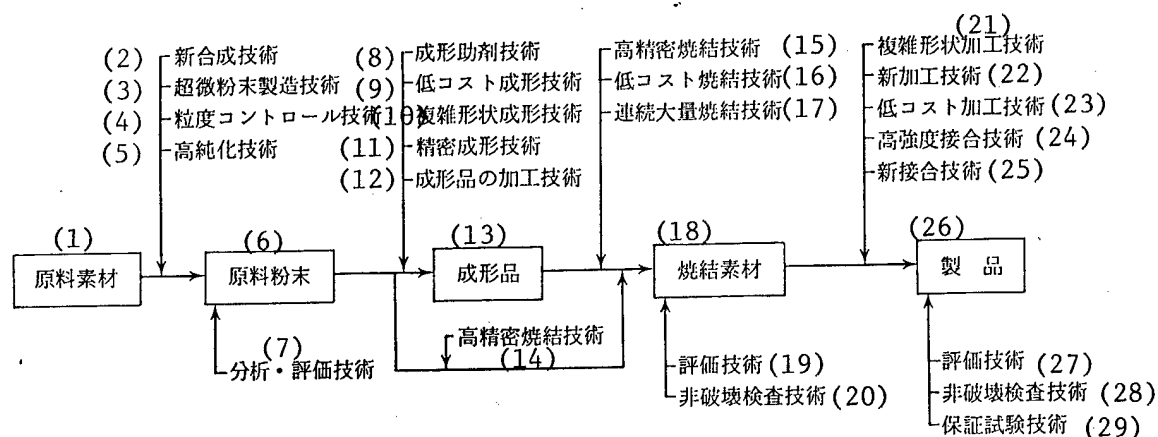
Since fine ceramics are generally difficult to process, the ceramic manufacturers are required to supply inexpensive ceramic parts in forms conforming to user specifications. So, forming technology is an important area of development. In the following outline of manufacturing processes, the themes of technological development will be explained.

The manufacturing processes of fine ceramics and the technologies required for respective processes are shown in Figure 4.

#### 5.1. Preparatory Process of Raw Material Powder

Since the ceramic powder of a diameter as small as a submicron is generally fit to obtain a high density sinter, the technology to produce ultrafine and highly pure powder is being developed. The solid phase reaction ( $\text{Si}_3\text{N}_4$ , SiC)

Figure 4. Technologies Required for Fine ceramics Production



Key:

- |                                           |                                           |
|-------------------------------------------|-------------------------------------------|
| 1. Raw material                           | 15. Same as above                         |
| 2. New synthesizing technology            | 16. Low cost sintering technology         |
| 3. Ultrafine powder production technology | 17. Continuous mass sintering technology  |
| 4. Particle size controlling technology   | 18. Sintered material                     |
| 5. Purity-upgrading technology            | 19. Evaluating technology                 |
| 6. Raw powder                             | 20. Non-destructive inspection technology |
| 7. Analyzing and evaluating technology    | 21. Complex shape finishing technology    |
| 8. Plasticizer technology                 | 22. New finishing technology              |
| 9. Low cost molding technology            | 23. Low cost finishing technology         |
| 10. Complex shape molding technology      | 24. High strength bonding technology      |
| 11. Precision molding technology          | 25. New bonding technology                |
| 12. Plastic solid processing technology   | 26. Product                               |
| 13. Molded material                       | 27. Evaluating technology                 |
| 14. High precision sintering technology   | 28. Non-destructive inspection technology |
|                                           | 29. Quality assurance test technology     |

and colloid chemistry ( $ZrO_2$ ) methods are prevalent. Upon completion of their development, these ceramic materials are reaching the stage of price competition. Meanwhile, the gas phase reaction method now at the stage of basic research is intended to secure high purity, controlled size, and ultrafiness of ceramic particles, and is an important theme for future development. At any rate, it is desired that a crystal phase, particle diameter, particle shape, and grain distribution can be constantly controlled and that the raw material powder can easily be available at cheap prices.

## 5.2. Plastic Process

Forming process is intended to take pulverulent materials and shape them into a specific product. There are many methods for this as shown in Table 4. The

Table 4. Molding Technologies of Various Kinds

Key:

1. Molding method
2. System
3. Shape of plastic solid
4. Mechanical press molding
5. Complex shapes
6. Hydrostatic pressure molding
7. Cold isostatic Pressing (CIP) system
8. Generally, simple shapes (applicable to complex shapes)
9. Cast molding
10. Slurry casting (dry casting, core casting), doctor blade
11. Complex shapes, forms of film and sheet
12. Extrusion molding
13. Ram system, screw system
14. Bars, pipes, basic materials with sections of abnormal shapes
15. Extrusion

|      |          |                                             |                       |
|------|----------|---------------------------------------------|-----------------------|
| (1)  | 成形法      | 方 (2) 式                                     | 成形品形状 (3)             |
| (4)  | 機械プレス成形法 |                                             | 複雑形状 (5)              |
| (6)  | 静水圧成形法   | 冷間静水圧加圧式 (CIP) 法 (7)<br>(ラバープレス法)           | 一般に単純形状 (複雑形状可) (8)   |
| (9)  | 鑄込成形法    | 泥漿鑄込法 (ドライキャストینگ, (10) キャスティング), ドクターブレード法 | 複雑形状, フィルム, シート状 (11) |
| (12) | 押出成形法    | (13) ラム式, スクリュー式                            | 棒, パイプ 異形断面素材 (14)    |
| (15) | 射出成形法    | プランジャ式 (16)<br>スクリューインライン式                  | 複雑形状 (17)             |

16. Plunger system. Screw in line system
17. Complex shapes

injection molding method of applying the plastics molding has been developed in recent years to form ceramic materials into parts of abnormal and complex shapes. Although this injection molding is a good forming method, it has a demerit in that heat treatment takes a long time to completely eliminate organic bonding agents before sintering.

Since the hydrostatic pressure formation method is ideal for isotropic pressure formation, it is used to mold large-sized products. The recent technological improvements in selecting materials for rubber molds and shape-designing permit to consideration the application of the above formation method as a (near-net) formation method to form parts into abnormal shapes.

The technology to form raw pulverulent materials into shapes close to the specified shapes of products while providing high packed density and ensuring even distribution of the materials to every portion is most important in the production of superior ceramics materials. Thus the development of such technology is being carried out widely.

### 5.3. Sintering Process

Sintering is the process of coagulation and agglomeration while heating powder or its plastic solids. Various methods are being applied to bake plastic solids.

In order to raise the density of ceramic plastic solids up to 50-55 percent, an approximate theoretical density, it is necessary to have it contract by

15-20 percent at a lineal contraction rate. During the course of shrinkage troubles occur like deformation, bends and breakage.

The development of the technology to provide continuous sintering, ensuring dimensional accuracy at reasonable terms is particularly important.

#### 5.4. Finishing Process

Generally, ceramics are inherently difficult to process because of hard and brittle characteristics and present difficulties in fine finishing. At present, diamond grindstones are frequently used in processing.

In order to raise the processing efficiency of ceramic materials examination is being conducted in many ways: the upgrading of mechanical rigidity of workpieces, selection of grindstones, the combined use of electromagnetism and the use of ultrasonic waves. Meanwhile, the cutting of ceramics with a diamond tool is also being attempted.

The development of finishing technology to ensure high precision of ceramics at reasonable prices is an important task.

In order to put ceramic products to practical use it is necessary to establish the technology to bond them with metals. The reasons that bonding ceramics with metals is difficult and: the breakage which occurs centering around the point of bond at thermal impact, thermal stress and thermal cycle under high temperatures due to the big differences between the two materials in the coefficient of thermal expansion and other characteristics. The development of the technology to provide highly strong bonding is a particularly important theme.

#### 5.5. Coating Process

In order to largely upgrade the characteristics of ceramic parts such as heat-resistance, anticorrosion, and abrasion-resistance, ceramic coating to cover parts faces with ceramic films is being examined, and in some fields (tools) it has been widely commercialized. Lately, in addition to the combination of the existing materials, many different combinations have been developed by planning qualities of the basic materials and the filming materials. The classification of the methods to make ceramic films is shown in Table 5.

The themes of technological development on fine ceramics in the future are consolidated in Table 6.

### 6. Present Status of National Projects in Foreign Countries

While the research and development of fine ceramics is exposed to fierce world competition, international development cooperation is being advanced between Japan, the United States, and West Germany, so it is a matter of importance how to balance competition and cooperation.

Table 5. List of Ceramic Thin Film Generation Methods

|              |              |                      |   |                                                                                                        |
|--------------|--------------|----------------------|---|--------------------------------------------------------------------------------------------------------|
| Gas phase    | [            | Chemical reaction    | [ | Chemical vapor deposition (CVD)<br>Chemical transit method<br>Wafer reaction method<br>Spraying method |
|              |              | Physical evaporation | [ | Vacuum evaporation method<br>Ion plating method<br>Sputtering method<br>Plasma method                  |
| Liquid phase | [            | Physical             | [ | Liquid phase epitaxy method<br>Solution epitax method (EGM)<br>(Capillary liquid phase epitaxy method) |
|              |              | Chemical reaction    | [ | Permeation method<br>Anode reaction method<br>Oxidation-reduction                                      |
| Solid phase  | - Solid body | - Solid reaction     | [ | Vapor film reaction method<br>Coating method<br>Precipitation reaction method<br>Proliferation         |

#### 6.1. Present Conditions in the United States

The development of a high efficiency gas turbines began in 1971 through the joint efforts of auto, electric and ceramic manufacturers, using the funds of ARPA (Advanced Research Project Agency) and ERDA (the predecessor of the present Department of Energy). With the target of developing an all ceramic high efficiency gas turbine having a capacity of 200 HP at an inlet temperature of 1,371°C, many technological achievements have been accomplished, but this development effort is now performed by the present AGT (advanced gas turbine) project.

The presently ongoing projects in the United States concern the development of AGT-100, AGT-101 and a heat insulating diesel engine. Lately, the United States appears to have become quite sensitive to the development activities in Japan and is likely to regard Japan as its strong competitor. The development project of an auto gas turbine in the United States is outlined in Table 7.

#### 6.2. Present Conditions in West Germany

With the support of the Ministry of Science and Technology (BMFT) of West Germany and under the leadership of Aerospace Research Institute (DFVLR), ceramic, auto and turbine manufacturers and universities have been jointly carrying out the research and development of an auto gas turbine since 1974.

Table 6. Fine Ceramics-related Technologies and Themes of Technological Development

- Production Technology and Peripheral Technology -

| Area                  | Item                               | Themes of Technological Development                                                                                                                                                                                                                                                                                             |                                                                                                                                                                                                                                                                                                                                                                   |
|-----------------------|------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                       |                                    | Directly Related Area                                                                                                                                                                                                                                                                                                           | Peripheral Area                                                                                                                                                                                                                                                                                                                                                   |
| Production Technology | Raw material production technology | <ul style="list-style-type: none"> <li>*Even particle powder production and control technology</li> <li>*Technology to secure ultra-high purity and ultrafine particles of raw materials</li> <li>*New technology to synthesize raw powder materials</li> <li>*Technology to develop resources</li> </ul>                       | <ul style="list-style-type: none"> <li>*Technology to analyze and evaluate fine ingredients</li> </ul>                                                                                                                                                                                                                                                            |
|                       | Molding technology                 | <ul style="list-style-type: none"> <li>*Development of technology and equipment to provide high precision complex shapes</li> <li>*Technology to mass-produce large-sized molded products</li> <li>*Development of high performance binders</li> <li>*Technology to finish molded products</li> </ul>                           | <ul style="list-style-type: none"> <li>*Advanced theorization of rheology for pulverulent materials</li> </ul>                                                                                                                                                                                                                                                    |
|                       | Sintering technology               | <ul style="list-style-type: none"> <li>*High precision sintering technology</li> <li>*Technology to mass sinter large-sized and complex-shaped products</li> <li>*Automated and continuously operating equipment</li> </ul>                                                                                                     | <ul style="list-style-type: none"> <li>*Technology concerning low energy-type high temperature furnaces</li> <li>*Development of refractory bodies</li> <li>*Technologies to control atmosphere (temperature, pressure, gas composition) and measure.</li> </ul>                                                                                                  |
|                       | Processing technology              | <ul style="list-style-type: none"> <li>*Technology to finish high precision complex shapes</li> <li>*Technology of mass-processing at low costs</li> <li>*Development of technology to finish causing no strain</li> <li>*Development of bonding and binding technology</li> <li>*Development of new binding methods</li> </ul> | <ul style="list-style-type: none"> <li>*Development of new process energy</li> <li>*To clarify relation between processed degenerated layers and physical properties of materials</li> <li>*Development of very fine and cheap abrasives</li> <li>*Superprecise printing technology</li> <li>*High precision mass production type measuring technology</li> </ul> |

|                       |                                                          |                                                                                                                                                                                                         |                                                                                                                                                                                                                                                                                                                        |
|-----------------------|----------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Evaluation technology | Technology to evaluate functions and physical properties | <ul style="list-style-type: none"> <li>Development of high precision evaluation technology and equipment</li> <li>Consolidation and expansion of physical properties data by unified systems</li> </ul> | <ul style="list-style-type: none"> <li>Standardization of methods to evaluate physical properties of basic materials</li> <li>Advanced theorization of methods to evaluate physical properties and functions</li> <li>Establishment of new evaluation theories in parallel with basic materials development</li> </ul> |
|                       |                                                          |                                                                                                                                                                                                         |                                                                                                                                                                                                                                                                                                                        |

Cooperative relations in this field with the United States came into being in 1979. The development project in West Germany of an auto gas turbine is outlined in Table 8.

Table 7. Auto Gas Turbine Development Program and Ceramics Applications in The United States

Key:

1. Year
2. Staged development and commercialization
3. National project
4. Technological development by private enterprises
5. Commercial production
6. 300,000-500,000 units
7. Ceramic parts
8. Moving blade: SiC, Si<sub>3</sub>N<sub>4</sub>  
Stationary blade: SiC, Si<sub>3</sub>N<sub>4</sub>  
Shroud: SiC, Si<sub>3</sub>N<sub>4</sub>, lithium aluminum silicate  
Scroll: SiC  
Burner: SiC  
Heat exchanger: Aluminum silicate, magnesium aluminum silicate

| (1) 年 代            | 1980                                                                                                                                                                                                                                                  | 1985 | 1990 |
|--------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|------|
| 開発・実用化のステップ<br>(2) | 国家プロジェクト<br>(3)                                                                                                                                                                                                                                       |      |      |
|                    | 企業・技術開発<br>(4)                                                                                                                                                                                                                                        |      |      |
| (7)<br>セラミックス部品    | 商業生産化<br>(5)                                                                                                                                                                                                                                          |      |      |
|                    | (6) 30万~50万台                                                                                                                                                                                                                                          |      |      |
|                    | 動 翼: SiC, Si <sub>3</sub> N <sub>4</sub><br>静 翼: SiC, Si <sub>3</sub> N <sub>4</sub><br>シュラウド: SiC, Si <sub>3</sub> N <sub>4</sub> , Lithium Aluminum Silicate<br>スクロール: SiC<br>燃 焼 器: SiC<br>熱 交 換 器: Aluminum Silicate, Magnesium Aluminum Silicate |      |      |

Table 8. Auto Gas Turbine Development Key: Project and Ceramics Applications in West Germany

|                 |                                                                                                                                                                                        |
|-----------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (1)<br>プログラム    | <ul style="list-style-type: none"> <li>第1期: 1974~1977. 3,000万ドイツマルク (官民各50%負担)</li> <li>第2期: 1978~1980. 6,000万ドイツマルク (官民各50%負担)</li> </ul>                                             |
| (3)<br>セラミックス部品 | 動 翼: 反応焼結 Si <sub>3</sub> N <sub>4</sub> をホットプレス Si <sub>3</sub> N <sub>4</sub> ハブに結合<br>燃 焼 器: 反応焼結 Si <sub>3</sub> N <sub>4</sub> , SiC<br>熱交換器: 反応焼結 Si <sub>3</sub> N <sub>4</sub> |

1. Program
2. Phase 1: 1974-1977  
DM 30,000,000  
(government and private sector share 50 percent each)  
Phase 2: 1978-1980  
DM 60,000,000  
(government and private sector share 50 percent each)
3. Ceramic parts

4. Moving blade: Connect hot pressed reaction sinter Si<sub>3</sub>N<sub>4</sub> with Si<sub>3</sub>N<sub>4</sub> hub  
Burner: Reaction sinter Si<sub>3</sub>N<sub>4</sub>, SiC; Heat exchanger: Reaction sinter Si<sub>3</sub>N<sub>4</sub>

### 6.3. Present Conditions in Japan

The Agency of Industrial Science and Technology started in 1978 the "research and development of a high efficiency gas turbine" as part of the so-called Moonlight Project, the project for developing energy-saving technology. The aim is to complete a composite power generating system having the turbine's inlet temperature of 1,500°C and a total thermal efficiency of more than 55 percent. Since there is no material other than ceramics which can stand a temperature of 1,500°C, this project ambitiously attempts to make the burner, stationary and moving blades and heat exchanger of the gas turbine, of ceramic materials. Table 9 outlines Japan's gas turbine project.

Table 9. Research and Development of High Efficiency Gas Turbine and Applications of Ceramics in Japan

Key:

1. Total efficiency
2. More than 55 percent
3. Turbine's inlet temperature
4. 1,500°C
5. Output of gas turbine
6. 100 MW
7. Research items of ceramics
  - \* R&D of SIALON
  - \* Development of fiber-reinforced ceramics
  - \* R&D of evaluation technology of ceramic materials
  - \* Designing, manufacturing and evaluating technologies of heat-resistant ceramic parts
9. Ceramic parts
10. \* Turbine blade:  $\text{Si}_3\text{N}_4$ 
  - \* Burner:  $\text{SiC}$ , reaction sinter  $\text{Si}_3\text{N}_4$
  - \* Radiation shield plate: reaction sinter  $\text{Si}_3\text{N}_4$

|     |                           |                                                                                                                                        |     |
|-----|---------------------------|----------------------------------------------------------------------------------------------------------------------------------------|-----|
| (1) | 総合効率                      | 55%以上                                                                                                                                  | (2) |
| (3) | タービン入口温度                  | 1,500°C                                                                                                                                | (4) |
| (5) | ガスタービン出力                  | 100 MW                                                                                                                                 | (6) |
|     | (7)<br>セラミックスの<br>研 究 項 目 | ・サイアロンの研究開発 (8)<br>・繊維強化セラミックスの開<br>発<br>・セラミック材料の評価技術<br>の研究開発<br>・耐熱セラミック部品の設計<br>・製造・評価技術                                           |     |
|     | (9)<br>セラミックス<br>部 品      | ・タービン翼: $\text{Si}_3\text{N}_4$ (10)<br>・燃 焼 器: $\text{SiC}$ , 反応焼結<br>$\text{Si}_3\text{N}_4$<br>・遮 熱 板: 反応焼結 $\text{Si}_3\text{N}_4$ |     |

Additionally, the "Research and Development System of the Next Generation Industrial Basic Technologies" was inaugurated in October 1981 under which the development of basic technologies such as raw powder synthesization, production, evaluation and application technologies is being carried out.

The Agency of Industrial Science and Technology and the Ministry of Education are positively stepping up as a matter of the highest priority the research and development of fine ceramics through industry-university-government cooperation.

### 7. Points at Issue, Outlook

Despite a wealth of characteristics superior to the existing metal materials, it must be recognized that fine ceramics are brittle materials. With the good

understanding of the breaking behavior of the brittle materials, it is important to cover the brittleness in making application designs.

The main factor of breakage of fine ceramics is primarily the stress concentration on an extremely small defective point existing on the surface and inside. It is important to establish the production technology to ensure that ceramics do not contain such a defect, and thus cause breakage. To this end, it is necessary to establish advanced technology to control each process concerning raw powder, forming, sintering, and finishing. In this connection, it may be necessary to reexamine each process from a new viewpoint disregarding the existing technologies.

The enhancement of reliability of ceramic materials by detecting defects without destructive tests secures the confidence of machine designers, leading to the promotion of ceramic application. Furthermore, the forecasting of the useful life and quality assurance tests are extremely important matters in the commercialization of ceramic products.

The development of designing techniques making the most of the characteristics of ceramic materials must be conducted based on the thorough understanding of these characteristics and through the exchange between mechanical design engineers and ceramic material engineers.

The creation of a system using ceramics alone is impossible. In many cases, it is thought that ceramics bonded with either metals or organic compounds will be used, so one of the important themes is to develop the technology to bond materials that have different characteristics.

With respect to fine ceramics, there are some that have already reached the stage of commercialization, but they are generally still in the stage of energetic research and development.

In order to commercialize fine ceramics, a development project extending over a period of several to 20 years must be mounted. It is expected that particular efforts will be exerted in the future to enhance their reliability as materials, upgrade evaluation and design technologies and reduce costs.

It seems that technological exchanges will be stepped up internationally at government and business levels so cooperation and competition will continue in parallel.

At any rate, it may be necessary to continue steady development efforts from a long-term perspective based on a new concept without being misled by the present ceramics fever, unable to escape the feeling of being somewhat "overheated."

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END