KAWASAKI STEEL TECHNICAL REPORT No. 44 June 2001

Highly-Functional Materials in the Chemical Business Field*


Yasunobu Iizuka
Staff Assistant General Manager, Business Planning & Control Dept., Chemical Div.


Toshihide Suzuki
General Manager, Chemical Lab., Technical Res. Labs.


Satoshi Gotoh
Dr. Eng., Senior Researcher, Iron Powder & Magnetic Material Lab., Technical Res. Labs.

Synopsis:

In the Chemical business field, some highly-functional materials have been developed and have been produced in addition to the main businesses of coal chemicals and iron oxide. These materials are such that they can be used in electronic equipment, systems and batteries having needs of smaller size and can meet the needs of lighter weight and environmental protection. Among these materials, magnetic materials, carbon materials, plastic composite stampable sheets and plastic alloy are selectively introduced.

1 Introduction

In the company's Chemical Business Div. and its related departments, two main businesses have been carried out. One is the manufacturing and marketing of chemical products for which coal tar produced as a by-product in the manufacturing of coke for blast furnaces is used as the main raw material. The other is the manufacturing and marketing of the iron oxide produced from waste acids discharged from the steel pickling process and the manufacturing and marketing of magnetic materials produced using the iron oxide as the raw material. Aside from the business field in which these raw materials produced in home plants are used, the Chemical Business Div. has made its way into the plastics business by setting its sights on automotive outer panels and structural members.

Among these three fields, chemical products have formed a stable market, while the other two fields feature high speeds of technological progress and, accordingly, the development of materials (development of the company's products) plays an important role. Examples of these materials are highly-functional soft magnetic materials, iron oxide and carbon materials to meet the demands for small-size, high-performance design of electronic parts and cells, non-fluorine resin compounds to meet the needs for global environmental conservation, and stampable sheets which support weight reductions of automobiles.

With respect to these latter two fields, this paper describes the features of the products developed by the company, the history of the development, and future directions of these products.

2 Iron Oxide and Highly-Functional Soft Magnetic Materials

Iron oxide produced from waste acids discharged from the steel pickling line provides high-purity products and is suitable for the raw material of soft ferrite, which is a high-performance magnetic material.

Soft ferrite has a specific resistance which is by far higher than metallic soft magnetic materials and shows excellent soft magnetic properties in the frequency range between several kilohertz and several hundred megahertz. Soft ferrite is used for the cores of high-frequency transformers, choke coils, noise filters, etc., and demand for soft ferrite for consumer-oriented electronic products, such as household electrical appliances, personal computers and take-it-with-you cellular phones tends to increase on a worldwide basis.

For this reason, in 1990 Kawatetsu Magnex Corp. (now Kawatetsu Ferrite Corp.) entered into the MnZn ferrite business, making the most of its advantage of integrated production from the raw material, i.e., iron oxide, to ferrite cores.

In order to meet demands for low cost, downsizing, and high-frequency and high-performance design, the

* Originally published in *Kawasaki Steel Giho*, **32**(2000)3, 274–276

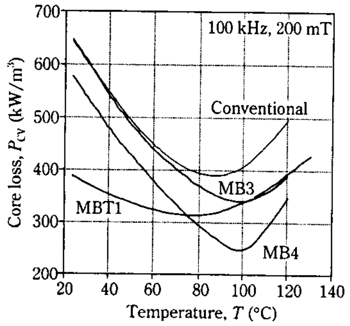

Fig. 1 Temperature dependence of core loss at 100 kHz and 200 mT of low loss materials, MB3, MB4 and MBT1 in comparison with the highest quality core manufactured by a conventional method

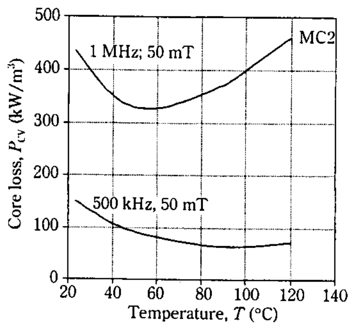

Fig. 2 Temperature dependence of core loss at 500 kHz and 1 MHz and 50 mT of MC2 developed for high frequency use

company's development department mainly carries out material development. It has developed four types of low-loss materials for switching power supplies and five types of high-permeability materials and has brought them into commercial production, and is putting its energies into meeting higher requirements.

First, low-loss materials for power supplies are described. In switching power supplies used in various electronic gears, technological innovation has advanced mainly toward downsizing and high-performance design and also in soft ferrite, which is a main component material of the transformer portion, low-loss design at high frequencies of not less than about 100 kHz is the centerpiece of technological innovation. The core loss of MnZn ferrite is composed of hysteresis losses, eddy current losses and residual losses, and when the switching frequency varies in the range 100 kHz to 1 MHz, the proportions of these three kinds of losses to each frequency vary. In consideration of this point, the company developed general-purpose low-loss materials for 100 kHz to 500 kHz, MB3[1], MB4[2] and MBT1, and a low-loss material for high frequencies of 500 kHz to 1 MHz, MC2. Effects of compositions and trace additives on the above factors of core loss in each frequency band and effects of manufacturing conditions and of crystal structure control, in particular, were quantitatively grasped and a core loss reduction was aimed at by optimizing them. **Figure 1** shows the temperature dependence of the standard core loss of MB4 and MBT1 in comparison with the core loss of the highest quality commercial material before the development of these low-loss materials. Further, the temperature dependence of the core loss of MC2 is shown in **Fig. 2**. Because MBT1 keeps low core losses in the range from room temperature to about 100°C, transformers which show low losses in a wide range of practical temperatures can be realized. Thus, MBT1 is a material which can meet social needs for energy savings.

Next, high-permeability materials are described. MnZn ferrite, which can provide the highest initial permeability among soft ferrites, is used in a relatively low frequency band of up to several megahertz or so. The company has also developed high-permeability materials with improved frequency characteristics MA055 to MA150 (with a specific initial permeability of 5 500 to 15 000) for the cores of noise filters and pulse transformers used in digital communications equipment, and has brought them into commercial production[3]. The frequency dependence of the initial permeability of these various kinds of high-permeability materials is shown in **Fig. 3**. In order to increase the initial permeability of a ferrite core, it is necessary to select a composition in which magnetic anisotropy and magnetostriction are zero. Furthermore, by making grains large and uniform it is important to form magnetic domain walls which can easily move and, at the same time, to select a material which is as free as possible from defects, pores, impurities, etc. within grains which impede the migration of magnetic domain walls. For this purpose, a high-purity iron oxide, KH-CPW[4], developed by the company, is used as the material. In addition, in order to improve the frequency characteristics of initial permeability and thereby to keep high permeability up to higher frequencies, it is necessary to suppress the core losses associated with an increase in frequency. Therefore, the fre-

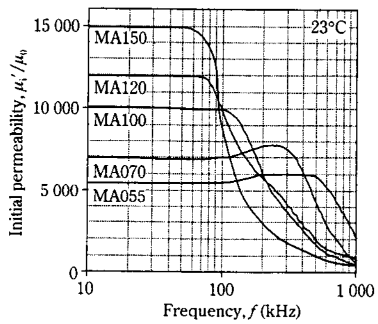

Fig. 3 Frequency dependence of initial permeability at 23°C of high permeability materials, MA055~MA150

quency characteristics were improved by the use of trace additives to precipitate at the grain boundaries and by reducing eddy current losses by increasing the resistance of the grain boundaries.

3 Carbon Materials

Coal tar products have formed large markets as tar pitch in the field of binders of artificial graphite electrodes, impregnating materials and electrodes for aluminum smelting and as middle distillates in the field of carbon black oils.

With the aim of increasing added value, along with these conventional markets, the commercialization of various kinds of high-grade carbon materials from tar pitch has been wrestled with. At the company, the commercialization of a spherical calcined powder "KMFC" has been come to grips with as one project for development of high-quality carbon materials. The manufacturing of KMFC involves separating and calcining mesophase spheres which are formed by the heat treatment of coal-tar pitch and have optical anisotropy. The size of KMFC is ten-odd micrometers in terms of average particle size, and KMFC is suitable as a material for high-density, high-strength carbon materials with self-sinterability. It was reported in 1977 by Yamada et al.[5] in the Kyushu Industrial Laboratory (now the Kyushu Industrial Research Institute) that KMFC can be separated by dissolving the pitch matrix in a solvent, and the company has succeeded in the industrial production of this material with its own technology for the first time in the world.

After that, it became apparent[6] that a graphitized product of this powder has excellent properties as the negative electrode material for Li ion secondary batteries, which have enjoyed high growth in association with the recent trend toward downsized and portable designs of electronic equipment, and in 1991 this powder was for the first time adopted for this application. Charge-discharge curves of KMFC are shown in **Fig. 4** as an example of its properties. As the performance required of a negative electrode material, current density, cycle

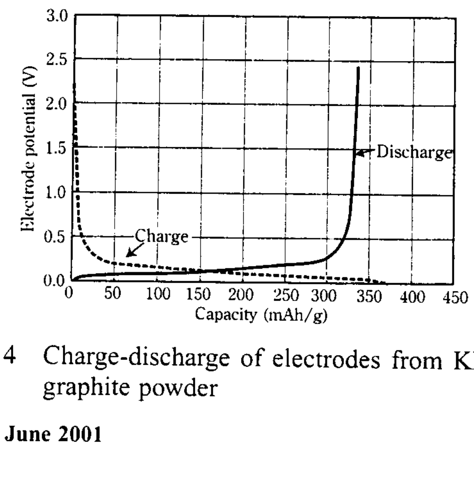

Fig. 4 Charge-discharge of electrodes from KMFC graphite powder

characteristic, etc., are mentioned in addition to charge and discharge capacity. At the company, negative electrode materials with improved performance have been developed and brought to the commercial stage. Furthermore, the development of high-performance products of negative electrode material on the basis of the accumulation of structure control technology of carbon materials has advanced into the field of non-graphite carbon materials with the objective of commercial production of next-generation high-performance materials.

4 Stampable Sheets

The company examined the commercial feasibility of automotive outer panels and structural members made of plastics. As one of the results of the examination, K-Plasheet Co. was set up in 1990 by the four companies Sumitomo Chemicals Co., C. Itoh & Co., Takiron Co., and Kawasaki Steel, which started the business of manufacturing and marketing of stampable sheets, which are thermoplastic resin compound materials. As the manufacturing technology, a process by the wet paper making process with foam was introduced from Arjo Wiggins, England, and industrialization was carried out on the basis of this process. This business was started from basic experiments on a demonstration plant in parallel with the establishment of operation techniques. In the development of materials and products, bumper beam systems for automobiles, etc., were aimed at by starting from flow molding applications. In the past several years, the targets of development have been shifted to expansion molding applications including interior trim materials by making the most of expandability, which is one of the features of the wet paper making process with foam. The manufacturing process of stampable sheets by the wet paper making process with foam comprises the step of forming a reinforcing material, called a web, from glass fiber and polypropylene, which is the matrix resin, and the step of forming this web into a sheet-like material by press forming. The sheet-like material, "KP-Sheet", thus produced, which is an intermediate base, is heated to a temperature not less than the melting point of the resin by a far-infrared radiation furnace, etc., given a prescribed shape within a die, and then cooled and solidified. The expanded porous composites of fiber-reinforced resin are obtained by making use of the phenomenon that expansion occurs during sheet heating by the springback of the fiber, i.e., a restoring force which works in such a manner that the fiber returns to the original condition of the web.

The features of the porous composites of fiber-reinforced resin as a material are mechanical properties with excellent plane stiffness and the function of a damper or insulator against various physical impulses. The former is utilized as a roof-lining material (**Photo 1**), which is one of the mainstays of K-Plasheet Co. In addition, KP-Sheet is also excellent in dimensional stability against

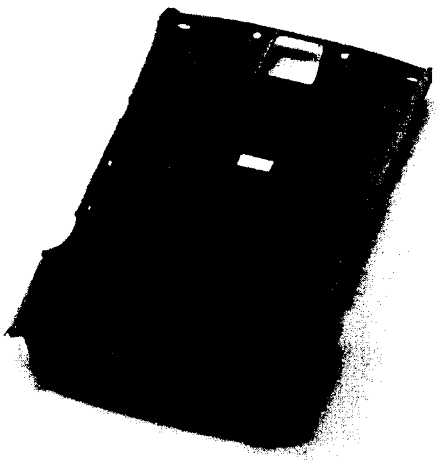

Photo 1 Headliner

temperature changes and humidity. For example, even when KP-Sheet is exposed to a condition of relative humidity (RH) of 95% all day long, the dimensional change is as small as less than 0.1%. This also applies when it is exposed to an atmosphere of 80°C. Furthermore, the elastic slope after exposure is almost the same as before exposure.

5 Polymer Alloys

Kawasaki Steel formed in 1991 Kawasaki LNP Inc., which has LNP Engineering Plastics Inc. and LNP Engineering Plastics Europe B. V. under its umbrella, and made inroads into the resin compound business. After that, in Asia, the company located a sales center in Singapore and a plant in Malaysia, smoothly increasing the sales of alloys in the Asian region. Furthermore, last year the company found its way into Brazil, thus further accelerating globalization. In the meantime, the company's development department has supported the global development of LNP by developing foundation technologies, contributing greatly to the development and improvement of LNP's products. Among other fruits, a sliding polycarbonate resin-based alloy "Lubriloy D" which will meet future environmental regulations is described below.

In recent years, sliding parts (gears, cams, etc.) of printers, copiers, etc. have tended to become larger in size in order to improve driving accuracy. For this reason, these parts are required to provide flame-retardancy and improved dimensional accuracy.

Conventionally, polyacetale widely used in this field has posed the problem that it is not compatible with flame-retardancy. On the other hand, polycarbonate/polytetrafluoroethylene (PTFE) sliding materials are expensive because they contain PTFE, although they can solve the problems of dimensional accuracy and flame-retardancy. In addition, PTFE sliding materials have the problems of low impact strength and inability to meet environmental regulations in Europe, etc. For these reasons, demands for polycarbonate-base sliding materials which do not contain PTFE are increasing. Therefore, the company started the development of polyolefin by noting its inexpensiveness. By ensuring the compatibility of polycarbonate and polyolefin, the company succeeded in developing an inexpensive and environmentally friendly plastic alloy which has equivalent slidability and provides impact strength more than three times the impact strength of PTFE (**Table 1**). At present, Kawasaki LNP Inc. is cultivating markets in America and Europe.

Table 1 Mechanical and tribological properties of Lubriloy (Lubriloy is the trademark of Kawasaki Chemical Holding Co., Inc.) D versus unfilled polycarbonate and standard 15% PTFE-lubricated polycarbonate

Property		Lubriloy D	DL-4030 PC, 15% PTFE	Polycarbonate
Specific gravity		1.17	1.28	1.20
Tensile strength	(MPa)	59	52	64
Elongation	(%)	60	60	90
Flexural strength	(MPa)	81	80	86
Flexural modulus	(GPa)	2.3	2.3	2.3
IZOD impact strength				
notched	(J/m)	750	270	900
unnotched	(J/m)	NB	NB	NB
HDT (1.8 MPa)	(°C)	127	127	130
LNP wear factor K (against steel)	(10^{-20} m^5-s/m-kg-s)	570	960	32 000
Static friction coefficient		0.04	0.03	0.31
Dynamic friction coefficient		0.07	0.06	0.38

6 Concluding Remarks

Functional materials developed and put into commercial production by the company in order to meet diverse demands in the chemical business field have been described. The authors intend to make efforts in the future to develop products capable of meeting further technological progress and social needs.

References

1) T. Narutani, H. Yoshimatsu, M. Yamazaki, K. Okutani, and K. Fujiwara: *Kawasaki Steel Giho*, **24**(1992)2, 150–151
2) H. Kobiki, T. Narutani, and K. Ikeda: *Kawasaki Steel Giho*, **29**(1997)4, 43–44
3) Kawatetsu Ferrite Corp.: Ferrite Core (Catalogue), (1997)
4) M. Tsuzaki, K. Takaki, F. Yoshikawa, and M. Shimasaki: *Kawasaki Steel Giho*, **24**(1992)2, 148–149
5) Y. Yamada, K. Sibata, and H. Honda: *Carbon*, **88**(1977), 2
6) K. Hoshino, T. Murakami, and A. Ootuka: *National Technical Report*, **40**(1994), 455