

KAWASAKI STEEL TECHNICAL REPORT

No.41 (October 1999)

*Advances in Iron and Steel Technologies,
Commemorating the 30th Anniversary of
Technical Research Laboratories*

Recent Activities in Reserach of Chemicals and Functional
Materials

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Synopsis :

In order to support the strategic operations of the Chemical Division of Kawasaki Steel, concerning mainly products, such as coal chemicals and plastic materials, the Chemical Laboratory has achieved various technical and product developments. Over the past years, the research has also been diversified to matters and articles in other fields, such as those pertaining to steel works, group companies and environmental protection. This paper describes some R&D results relating to the fluidized-bed catalyst for phthalic anhydride, meso-carbon microbeads for the negative electrode of Li ion secondary battery and plastic composite stampable sheets.

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In order to support the strategic operations of the Chemical Division of Kawasaki Steel, concerning mainly products, such as coal chemicals and plastic materials, the Chemical Laboratory has achieved various technical and product developments. Over the past years, the research has also been diversified to matters and articles in other fields, such as those pertaining to steel works, group companies and environmental protection. This paper describes some R&D results relating to the fluidized-bed catalyst for phthalic anhydride, meso-carbon microbeads for the negative electrode of Li ion secondary battery and plastic composite stampable sheets.

1 Preface

The Chemical Research Group of Kawasaki Steel was inaugurated in 1983 with the Resources and Energy Laboratory of the company and Technology Development Department of Kawatetsu Chemical Co., Ltd. as the parent organizations. Since then, the group has been engaged in R&D aiming at supporting work-site operation of the company's chemistry related business and exploring new fields of business as the two main wheels of its research activities. There have been big changes in the R&D environment in these ten years, however, we have integrated and reorganized our R&D themes responding to these changes.

Among the various items of research in progress in the group, the major topics this paper describes are those studies related to the production of phthalic anhydride, those related to development of stampable sheets and those related to production and application of spherulites.

2 R&D on Catalysts for Production of Phthalic Anhydride

The company has been producing about 30 000 t/y of phthalic anhydride by means of a fluidized-bed oxidation process using naphthalene as a raw material. We use vanadium pentoxide on a silica support (V_2O_5/SiO_2) as a catalyst and oxidize the raw material by air at about

350°C. As to the function of this catalyst, it is said that V_2O_5 , the active component, acts on $K_2S_2O_7$ ($\rightleftharpoons K_2SO_4 + SO_3$) in an eutectic state, however, while the catalyst is actually in use, various phenomena including a decrease in fluidity and deterioration in the activity occur. Therefore, we have been working to determine the cause of these phenomena, investigating countermeasures and improving and developing catalysts for some ten years.

In the initial stage of operation of the facilities, we were using crushed-type catalyst A, made by crushing active-element-impregnated silica carriers. This catalyst was imported from USA. The problems with this catalyst were that too much abrasion and dispersion of the catalyst itself occurred and time deterioration of its activity was severe. As a result of our analysis, we found that iron (Fe) gradually mixed into the catalyst resulting in the formation of $K_3Fe(SO_4)_3$ crystals, thus the catalyst became unable to take on the eutectic state needed for the appearance of the catalytic function. It was found that the mixing of Fe occurred due to the angular crushed-type catalyst grinding and wearing the vessel's wall, therefore, we studied how to make the catalyst spherical. By maintaining nearly the same composition as catalyst A, we developed the microspherical catalyst B prepared by the sol-mixed spray method and entirely replaced the catalyst used in commercial plants. Since then, we found almost no $K_3Fe(SO_4)_3$ in the catalyst.¹⁾

* Originally published in *Kawasaki Steel Giho*, 31(1999)1, 71-75

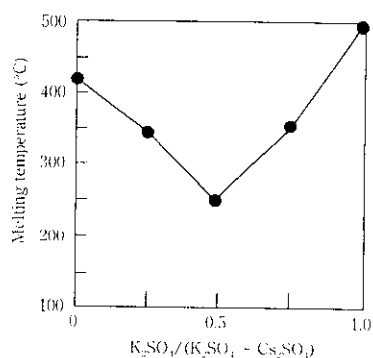


Fig. 1 Effect of $K_2SO_4/(K_2SO_4 + Cs_2SO_4)$ mass ratio on melting temperature of active components

Catalyst B showed high wear resistance and its initial activity was also high, however, the fluidity gradually decreased while in use. When we examined catalyst B using an EPMA (electron probe microanalyzer), it was found that the elements forming active components gravitated to the external surface and the S/K ratio on the external surface was reduced. It was inferred that SO_3 volatilized from $K_2S_2O_7$, a component forming eutectic material, and formed K_2SO_4 having a high melting point. The above phenomena were presumably caused by a part of the surface of the thus-formed K_2SO_4 being solidified and particles agglomerating. Therefore, we developed catalyst C with the melting point of the sulfate being lowered by substituting a part of the K with Cs. The relationship between the K/Cs ratio and the melting point is shown in Fig. 1 and the compositions of catalysts B and C are shown in Table 1. When catalyst C was used in commercial plants as a replenisher for catalyst B which is apt to wear and disperse by itself, the fluidity recovered. The activity of catalyst C was also found to be higher by about 20% than that of catalyst B.^{2,3)}

As the percentage of catalyst C in the reaction vessel further increased, the fluidity dropped again. We judged that this indicated that there should be an optimum point in the K/Cs ratio, therefore, we experimentally prepared many samples of catalyst with different ratios and evaluated these samples. As a result, we found that as the content of the Cs increases, the eutectic point drops and the catalyst easily reaches an eutectic state at the reaction temperature, however, the viscosity of the eutectic mixture increases. We also found that the optimum composition is different for fluidity and for reactivity. For these reasons, we investigated whether we could satisfy various requirements by mixing catalysts B and C depending on the circumstances rather than introducing a new catalyst with an optimized K/Cs ratio. We performed oxidization tests using a mixture of catalyst B (without Cs) and catalyst C (with Cs) with a ratio of 1:3 and periodically analyzed the catalyst using EPMA by

Table 1 Composition of B and C catalysts (%)

	B catalyst	C catalyst
V_2O_5	4	4
K_2SO_4	15	7.5
Cs_2SO_4	0	7.5
SO_3	5	5
SiO_2	Balance	Balance

sampling a part of it. In one quarter of all particles measured immediately after mixing, Cs was not detected, however, Cs was detected in all particles measured after one day or more from the beginning of the reaction. We found that the standard deviation of the K/Cs ratio of each particle decreases with time and the K/Cs ratio of each particle equalizes. From the fact that we observed the active components gravitating towards the external surface of the catalyst particles through EPMA spectra analysis and SEM (scanning electron microscope) photographs, it can be inferred that the active components move between the catalyst both ways during reaction and gradually equalize.⁴⁾ Utilizing this phenomenon, it has become possible to maintain fluidity for a long period of time in commercial plants by replenishing the catalyst with catalyst B or C alone or with a mixture of the two depending on the circumstances.

3 Development Studies on KMFC (Kawasaki Mesophase Fine Carbon)

Kawasaki Steel is a leading tar distillation producer using coal tar produced as a byproduct of steel production as the raw material and has been carrying-out R&D aiming at increasing the added value of the tar pitch. We paid attention to the studies of Yamada *et al.*⁵⁾ on mesophase spheres and succeeded in the development of KMFC by advancing our studies from fundamental research to industrial research. As a result, we started production and sale of KMFC in 1987 for application to high density and high strength carbon materials needing self-sinterability. Furthermore, it was made clear recently that KMFC graphite powder shows superior characteristics as a negative electrode material for lithium ion secondary batteries and we have been using spherulitic graphite powder for these electrodes since 1991.

The special feature of KMFC is that it is self-sinterable due to the presence of the binder components, toluene insoluble and quinoline soluble β -components, remaining in optically anisotropic spheres. In order to make this feature appear, the production process is composed of a heat-treatment process, a solvent extraction and filtration process, a drying and calcination process and a classification process.^{6,7)} In R&D related to the series of these processes, we have investigated the control of self-sinterability due to the presence of β -components together with the mechanism of self-sintering. As

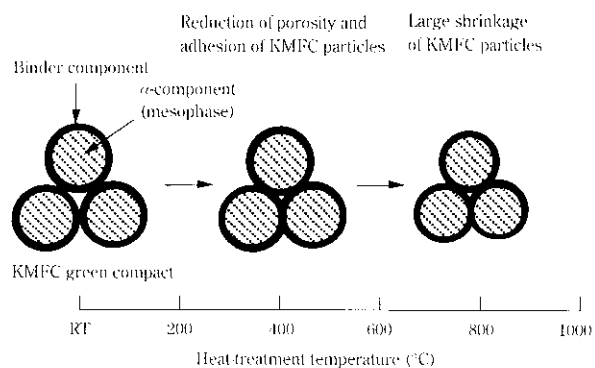


Fig. 2 A model of sintering mechanism of KMFC green compact

shown in Fig. 2, self-sintering of KMFC may be understood to progress in the two temperature ranges of 400-600°C and over 600°C. First of all, KMFC is densely filled as a green compact by molding. At temperatures between 400°C and 600°C, the size of the pores in the green compact is reduced as the β -component adjusted through the calcination process melts and at the same time, sintering between KMFC particles progresses. At temperatures above 600°C, growth of the hexagonal structure and densification of the stacking structure progress and shrinkage of KMFC particles themselves progresses.⁸⁾ We have thus clarified that carbon materials of high density and high strength can be produced without using any binder.

As KMFC is a graphitizable fine carbonaceous powder, it was reported by Hoshino *et al.*⁹⁾ and Tatsumi *et al.*¹⁰⁾ recently that it exhibits excellent characteristics as a raw material for the negative electrode of lithium ion secondary batteries. For this application, KMFC is graphitized without being molded and is used in a fine particle form. Recently, we have been doing R&D on KMFC also to improve its performance as a raw material for negative electrodes in addition to studies on using it as a raw material for carbon materials of high density and high strength.

Kawasaki Steel has been doing R&D to further stabilize and improve the quality on the basis of technologies fostered over many years and to satisfy various requirements raised by our customers for various applications.

4 Studies on Stampable Sheets

We established K-Plasheet Co., in February, 1990 as a joint venture with three other companies, Sumitomo Chemicals Co., C. Itou Co. and Takiron Co. and are producing and selling stampable sheets, a type of thermoplastic resin compound.¹¹⁾ Historically R&D started with basic experiments to establish operation technology in commercial plants on the basis of stampable sheet production method by means of the wet paper making process with foam originated and introduced by Arjo

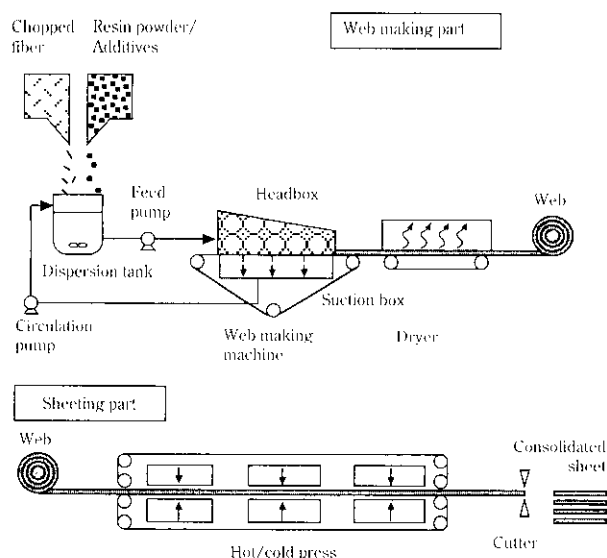


Fig. 3 Schematic illustration of the manufacturing process of stampable sheet with paper making method¹²⁾

Wiggins Co. in U.K. Development of the materials and products began with exploitation of flow molding applications represented by automotive bumper beam system, and the objective has been shifted to expansion molding applications including interior trim materials for automobiles by making the most of the expansibility which is a distinguished feature of stampable sheets produced by the wet paper making process with foam.

Figure 3 shows the outline of the stampable sheet production process by the wet paper making process with foam. The production process is composed of a process to form a twisted mixture of PP which is a strengthening material called the web and is made of glass fiber and matrix resin and a process to make the twisted mixture into consolidated sheets using a thermal press.

The basic characteristics of the web, i.e. fiber orientation and surface appearance, are determined by the flow field and suction pattern of the foamed slurry in the head box. On the basis of flow analysis on the foamed slurry which is a compressive fluid and the test results using a wet paper making model machine, we improved the head box and manifold of commercial plants and have established quality control methods for commercial plants so that the width-wise variance of grammage is reduced and fiber orientation is controlled.¹²⁾

In the thermal press process, on the other hand, we have clarified from heat transfer calculations, model simulations of material properties and experiments that the heat conduction in a web made of porous composite is dominated by heat conductance between the web and the press plate and that the basic structure formed by sufficiently impregnating resin between reinforcing fibers governs the material properties of the final prod-

ucts. From the two aspects of improving productivity and improving quality, the results have been fed back to help optimize various operating parameters of commercial plants such as temperature and pressure.

In the initial stage of development, we performed design and development of stampable sheet materials of various grades including high tensile, uni-directional and fine surface appearance grades focusing on semi-structural members of automobiles. Thereafter, however, we shifted our objective to developing materials for expansion molding which would make it possible to obtain fiber reinforced resin porous composites by making use of the springback of fibers which occurs when the sheets are heated.

The special features of fiber reinforced resin porous composites as a material are mechanical properties superior in plane stiffness and damping or insulator functions against various kinds of impulses. Our main product at present is roof-lining material for automobiles.

Through the process of development, we have accumulated results to standardize the design processes and as know-how by clearly defining the relationship between the commercial properties of products and the basic properties of materials and also by narrowing down the factors governing these properties. Furthermore, our molding and processing technology including flow analysis, etc. and our product designing technology including structural analysis, heat vibration analysis, etc. have also become indispensable for developing applications. Through our studies to develop analytical methods made by taking various unique material properties of resin compound materials such as visco-elastic and elastic-plastic behaviors into consideration, we have evaluated various commercial properties such as the impact properties of long fiber reinforced materials which can be differentiable factors for the products¹³⁾ and at the same time, we have been feeding the results of our eval-

uation back into development of new materials.

With respect to themes for R&D, we have already started our studies with the recycling of parts becoming serious in the year 2000 and therefore, however, to establish the total system also including thermal recycling will be one of the important themes together with confirmation of material recyclability and development of recycled products. In the aspect of material development, on the other hand, to develop new compounds and to develop material design technology as well as joining and adhesion technology which support combinations of these compounds with other materials will be the major props of our development work.

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