1. Background to the Establishment of the Research Project

In recent years, the Far East iron and steel manufacturing industry has been developing at a rapid pace, and as a result iron ore is now in short supply. Iron ore is a heavy bulky material, and transporting it entails considerable expenditure as well as the use of diverse types of equipment. Consequently, the Far East region is highly dependent on the use of Australian iron ore which is transported to and processed in coastal steelworks. These conditions are exacerbating the existing problems of Australian iron ore as associated with the depletion of high-grade hematite deposits, and are speeding up the fresh exploitation of lower-grade limonite deposits. Japan’s integrated steel industries was thought hard to be produced satisfactorily, because Marra Mamba ore having high combined water content and high porosity was expected unsuitable for sintering. Therefore, the method of using goethite had been studied and the combination with low slag ratio important for melting behavior of goethite was investigated.

Each university had been engaged in basic research such as granulation, agglomeration, evaluation of reaction in a blast furnace to propose a new process for “porous meso-mosaic texture sinter” which was anticipated simultaneously to realize high strength and high reducibility under the conditions of low slag and high goethite ratio in sintering.

By combining these basic researches, the theory of agglomeration and the engineering foundation for raw material/sintering/blast furnace process were discussed and a new process for “porous meso-mosaic texture sinter” based on improving granulation process of raw material was searched. As a result, proposed was the MEBIOS (Mosaic Embedding Iron Ore Sintering) method which involved arranging dense pre-granulated pellets (firing cured bed) in a sinter induction bed with a raw material composition capable of forming a suitable void network under normal sintering conditions.

KEY WORDS: ironmaking; agglomeration; granulation; sintering; goethite; simulation; phase diagram; texture.
into the blast furnace, and increasing the quality or production levels of sinter is thought to contribute significantly to reducing the ratio of reducing agents in blast furnaces. When a transition was made from magnetite ores to hematite ores as the raw material for sintering, self-fluxing sinter was developed and, as a result, the reduction of reducing agent ratios to 150 kg/p-t and above was recorded for the first time. The sintering of goethite/limonite ore as the starting mineral is thought to be very useful for forming a micro-porous texture that is highly suitable for gaseous reduction reactions. Also, indications are that the limonite beds scheduled for fresh development in the future consist not of pisolite which has a high SiO₂ content, but of Marra Mamba which has a relatively low SiO₂ content. Marra Mamba ore is thus advantageous when aiming for a sinter that has a strong porous texture with low slag content, and there is a rapidly growing demand for the development of techniques that use such ores (Fig. 3).

2. Research Project Activities

In this research project, assuming the mixing of large amount of limonite ore and low slag ratio as the raw materials for the sinter production, we set out with the aim of conducting pioneering research into sinter process technology in order to reach the targets of achieving improved quality while maintaining and increasing the productivity of sinter production by exploiting the characteristics of Marra Mamba limonite.1) The research activities were divided into three areas: (a) texture design of sinter quality, (b) process design of sinter production, and (c) design of systems for practical applications. With regard to (a) and (b), research was mainly conducted by highly specialized university-based committee members into the four basic themes that form the key points of each area (Fig. 4). As for (c), a working group (WG) was formed by industry researchers and university-based committee members with a thorough knowledge of the actual state of sinter production. This WG studied the systems and sinter production processes that determine the issues addressed by the research project, and implemented research into the realization and application of individual technologies developed in this project, covering (i) organization of existing research/technology issues and establishment of research themes, (ii) evaluation of Marra Mamba ore, (iii) investigation of applied technology for resolving the issues, and (iv) proposal of new processes and extraction of research topics (Fig. 5).

In concrete terms, the members of this WG engaged in free discussions on process concepts for maintaining or improving the sinter productivity in situations where there is
increased use of ores with a high content of combined water, such as pisolitic ores and Marra Mamba ore. As a result, two methods were deemed worth investigating: preliminary dehydration treatment of ores with a high content of combined water, and enhancement of the sintering bed structure control. With regard to the former (preliminary dehydration of ores with a high combined water content), the main points of discussion were what preliminary heating temperature is needed (whether or not preliminary compacting is needed), and where the heat source can be obtained from. With regard to the latter, problems were identified with processes such as preliminary granulation and raw material loading. **Figure 6** outlines a process in which both are taken into consideration.

### 3. Aims and Achievements of Each Research Theme

#### 3.1. Basic Research into Evaluating the Sinter Texture

##### 3.1.1. Targets for Texture Design Relating to the Sinter Quality

With regard to the quality of sinter charged into blast furnaces, the following attributes are required: it should have a lump size of 5–100 mm with no fine content, it should maintain its strength and should not soften or shrink during the reduction process, even at a temperature of 1 200°C, it should be capable of reducing from iron oxide to iron without difficulty, and slag should be small in quantity and should be able to drop down without difficulty. Factors that can be used to evaluate these quality requirements are the cold strength, reduction degradation properties, reducibility, softening properties, and chemical composition. Sinter is made by crushing and grading sinter cake, in which there are pores and voids that can be classified into three types according to the functional size. In decreasing order of size, these are as follows: (i) ‘voids’ of 5 mm or larger through which the ventilation flue gas is able to flow, (ii) spherical ‘pores’ inside the sinter through which the ventilation gas cannot flow, and (iii) aspherical ‘micro-pores’ that exist in the gaps between crystals and resemble defects inside crystal grains. To obtain porous materials with greater strength, it is preferable to reduce the level of structural defects (voids, pores and micro-pores), but the most important prerequisite for current iron ore sintering processes based on convective heat transfer is that there are ventilation voids present inside the sinter cake. Next, the basis of pore design in the quality of sinter is to promote gaseous reduction reactions while maintaining the strength, i.e., to improve reducibility while maintaining the cold strength, reduction degradation properties and load softening properties.3) Basically, the design process involves reconciling apparently conflicting properties. Different pore sizes seem to have different effects on the cold strength and high-temperature reducibility, with the high-temperature reducing properties governed by the micro-pore structure and the cold strength governed by the pore structure (excluding micro-pores). A suitable structure must therefore be designed by taking these differences of scale into account.

Also, the chemical composition does not simply determine the composition and quantity of slag produced in the blast furnace, but is also an important factor in determining not only the pore structure but also the mineral texture that governs the reactions (reduction, melting, softening) that the sinter is subjected to inside the blast furnace. In this research project, texture design was studied based on the prerequisite of reducing slag constituents (SiO₂, CaO) in sinter which has recently been promoted in real production (**Fig. 7**). Recent efforts to reduce the slag constituents of sinter have tended to reduce the amount of calcium ferrite minerals with multiple constituents (SCFA) and silicate-based slag minerals while increasing the iron oxide content, and under these conditions, therefore, it is essential to assess how the formation of mineral textures and the reducibility of sinter will be affected by Al₂O₃, MgO, and FeO constituents.5) Since a lower liquid phase ratio of iron oxide is needed in sintering reactions with fewer slag constituents (SiO₂, CaO) in the saturated state, we focused on FeO constituents as substitute constituents. Here, we concentrated on evaluating the reducibility of iron oxide minerals (Fe₂O₃, FeO·Fe₂O₃, FeO), especially the high-temperature reducibility with the coexisting liquid phase.
3.1.2. Research Achievements Relating to Improvement of Reduction Properties

(Research theme 1): Evaluating the reducibility of sinter with a high FeO content [Nakazato]
(Research theme 2): Clarifying the solid solution modes and limiting quantities of Al₂O₃, MgO and SiO₂ constituents related to calcium ferrite minerals with multiple constituents (SFCA) [Sugiyama]

In the evaluation of low-temperature reducing properties of individual constituent minerals of sinter at 900°C, it was found that hardly any reduction takes place in silicate slag minerals containing FeO, such as 2FeO·SiO₂ and FeO·SiO₂·CaO minerals (Fig. 8). It is thus important to avoid the formation of such minerals. For this purpose, the SiO₂ constituents basically have to be reduced at the blending stage if there is a high proportion of FeO constituents in the sintering melt. Next, to prevent SiO₂ constituents from forming 2FeO·SiO₂ minerals or FeO·SiO₂·CaO minerals, the CaO/SiO₂ ratio of the composition should be set to more than 2 so that the 2CaO·SiO₂ minerals crystallize out, and the proportion of MgO constituents or Al₂O₃ constituents should be increased to raise the SiO₂ solid solution capacity of SFCA and the amount of this material formed (Fig. 9). The presence of Al₂O₃, CaO and MgO constituents is thus advantageous when there is a high SiO₂ content, whereas the presence of FeO is undesirable.

In the evaluation of high-temperature reducibility at 1200°C, it was found that melts produced by melting rather than by the additive evaluation of single minerals exhibit a phenomenon whereby the iron oxide is surrounded and the reduction stagnates. This phenomenon is affected by the pore structure and permeability of the reducing low-melting-point melt of the sinter texture and by the generated quantity thereof. The composition of the low-melting-point melt was based on FeO·SiO₂, and the addition of Al₂O₃ improved the reducibility while the addition of CaO (CaO/SiO₂ = 1) caused it to decrease.

The reduction degradation of sinter in the blast furnace originates from the expansion stress that occurs when hematite minerals undergo gaseous reduction into magnetite minerals, resulting in the formation of minute cracks around the hematite mineral. Increasing the amount of hematite material and dispersing the hematite material inside the sinter texture thus promote the reduction degradation properties. Accordingly, the reduction degradation properties are increased by promoting the formation of iron oxide minerals by reducing the slag content and by blending in large amounts of limonite-based minerals with favorable sinter reaction properties and dispersing them into the hematite mineral texture. However, it is thought that the reaction participation of FeO components that results from the addition of MgO components and strengthening of the reducing atmosphere promotes the formation of FeO·Fe₂O₃ minerals and MgO·Fe₂O₃ minerals and suppresses the formation of Fe₂O₃ (hematite) minerals, thereby allowing the reduction degradation properties to be maintained or even improved.

3.1.3. Research Achievements Relating to Maintaining Cold Strength

(Research theme 3): Strength evaluation of meso-porous sinter textures [Aizawa]
(Research theme 4): Pore formation behavior in the melt-
ing assimilation process, and evaluation of local strains in the resulting iron oxide [Sasaki].

Limonite-based ores characteristically contain combined water and large numbers of pores in their original form, and subjecting them to thermal processing results in a highly reactive material with cracks (low strength) and pores (micro-pores). When an iron ore of this type is blended in large quantities in the sinter production, the assimilation reaction of the iron ore particles with the resulting melt is naturally speeded up, making it more receptive to processes such as the formation of pores and micro-pores, which has a large effect on the cold strength. Accordingly, in order to understand the sinter strength of limonite-based ores, it is necessary to clarify at a microscopic level how pores are formed after thermal decomposition of the limonite and the behavior of the assimilation reaction. Also, with regard to reducing the amount of slag produced by sinter, it is not easy to realize cold strength by reducing the proportion of liquid phase. Therefore, in order to clarify the pore distribution mode and the limiting pore size needed to maintain strength, we developed a system that can analyze the strength of sinter by producing computer models of pore unit cells based on photographs of the sinter texture (Fig. 10). With this system it became possible to evaluate the overall strength based on real or virtual photographs of sinter textures.

Also, as a result of using EBSP (electron back-scattering) to study the residual strains that remain in the mineral texture of sinter, we found that there are residual strains within 10 μm of the grain boundaries but no residual strains at greater depths inside the grains (Fig. 11). From this result it is inferred that a strain distribution exists in sinter crystal grains measuring 20 μm or more, making them liable to fracture when subjected to external stress. The relationship between the limiting pore size and the limiting crystal grain size that affects the strength of the ore cannot be stated simply, but as a rough ballpark figure it is judged that the effect limit size of pores is also in the region of 20 μm.

The sinter texture basically consists of an unmolten solid phase, a resolidified solid phase, and pores. By studying the mineral texture around the pores, it was inferred that pores with a large size are related to the resolidified solid phase and pores with a small size are related to the unmolten solid phase. Measurements also showed that the pore diameter is 20 μm or less after heat treatment, suggesting that even if the limonite grains are dispersed and assimilated, the micro-pores remain if it stays as an unmolten solid phase.

From observations of the assimilation behavior of CaO and hematite plate surfaces, it was pointed out that even when there is abundant CaO · Fe₂O₃ melt available, the integration and growth of pores is not determined only by the physical properties of the melt, but is also related to solid-phase migration due to permeation inside the hematite plates toward the hematite crystal grains. It is also thought that when pores become suspended in the melt, the pore migration distance is very small and even after a long time has passed it is difficult for them to combine and become coarser. In other words, to make the pores combine and become coarser, it is not the melt viscosity or the holding time between the end of melting and resolidification that is important, but the time from the formation of the initial melt until the end of melting (i.e., the melt formation rate). Put simply, one might say that the time taken for the solid particles to form a melt has an important bearing on pore formation, and that only a small amount of integration of pores occurs between the end of the melting period and the resolidification of the melt.

Thus, under conditions where a large amount of limonite ore is blended in, the micro-pores readily remain, which is effective at improving the reducibility. Also, to suppress the formation of pores in the sinter and obtain a sintered cake with rougher voids and greater strength, it is thought that the melting assimilation speed should be decreased rather than simply prolonging the high-temperature holding time, and that it is effective to make the raw material particles coarser or finer and to reduce the rate at which the temperature is increased. In other words, to prevent an increase in porosity when using limonite ore, it is necessary to develop granulation techniques that make the raw material particles coarser or finer.
3.2. Basic Research Relating to Sinter Production

3.2.1. Viewpoints Relating to Process Design for Sinter Production

Since limonite-based ores contain a lot of combined water and are porous, they have a low bulk density when used as raw materials for sintering, and their sintering productivity and sinter cake strength (product yield) are also worse (Fig. 12). Furthermore, since this ore is porous and highly reactive, it has favorable melting assimilation properties and improves the melt viscosity (solid phase ratio), and tends to have worse sintering bed ventilation properties and sinter cake strength. Also, since reducing the level of slag constituents in the sinter involves reducing the level of CaO constituents which act as a solvent, the melt viscosity tends to increase further still, and the sinter bed ventilation properties and sinter cake strength are impaired. Accordingly, there are major technical issues involved in maintaining production yield and maintaining or improving the sintering productivity in the production of sinter with low slag constituents that contains a large proportion of limonite.

To overcome this problem, a suitable quantitative design should be conducted into the structural formation of sinter cake and the assimilation behavior of sinter melting based on a thorough understanding of the melt viscosity (solid phase ratio)\(^{(15)}\) and a thorough understanding of the melting assimilation of limonite ore.

Hitherto, in studies relating to the evaluation of sintering raw materials, considerable effort has been put into simulation experiments using the sinter pot test method and basic experiments in which sintering is performed in electric kilns by introducing model raw materials into a crucible. However, when considering composite granulation sintering methods in which the raw materials are not simply uniformly blended together but their distribution is taken into account, the degrees of freedom become unlimited and studies that rely on experimental trial-and-error methods are of little use. Attention was therefore turned to studies using numerical simulation techniques.

In earlier raw material evaluation studies based on mathematical models, the sinter melting assimilation ratio was estimated by a single interface reaction model where the porosity of the assimilated particles was assumed to have a linear rate, and the porosity, void ratio and bed contraction rate were estimated from the reaction composition.\(^{(15)}\) Attempts have also been made to analyze clustering structures by determining the liquid phase ratio from the temperature and composition of the melting assimilation parts by means of a dispersed element simulation method.\(^{(16)}\) Simulation designs and analytical studies based on mathematical models of this sort are important techniques not only for promoting the scientific clarification of sintering processes, but also for determining which design factors should be optimized, such as packing density, melting assimilation ratio, melt viscosity, and sinter cake structure.\(^{(17)}\)

We therefore prepared a liquid phase diagram of the Fe\(_2\)O\(_3\)-FeO-CaO-SiO\(_2\)-MgO-Al\(_2\)O\(_3\) system which is essential for performing quantitative design studies, and we prepared parameters relating to the formation of pores and voids and to the melting assimilation behavior of limonite-based ores under low slag conditions.

Furthermore, as the most important parameter for controlling the sintering reaction, we focused on the grain size and apparent density (porosity) of the granulated material, and with regard to the related granulation phenomena we performed a quantitative study of the physical properties of limonite and the specifications of granulation equipment. Quantitative studies of the granulation of sinter raw materials have mainly been performed as simulated laboratory-scale experiments,\(^{(18)}\) but the basic laws governing dimensional properties such as the dissimilarity between the particle dimensions and equipment dimensions are unclear. In any case, mathematical models simply link parameters together with model experiment formulae, and have limited scope for development in terms of their practical application and theoretical utility. There thus seems to be a need for process design and analysis of granulation phenomena using numerical simulation techniques based on general theory. With regard to the physical properties of limonite ore, we studied the structural analysis of granulated material particles, and with regard to the specifications of granulation equipment we studied the analysis of particle movement of granulated materials by means of the discrete element method (DEM).

3.2.2. Research Results Relating to Sinter Assimilation Reactions and Ventilation Void Structure

(Research theme 5): Fe\(_2\)O\(_3\)-FeO-CaO-SiO\(_2\)-MgO-Al\(_2\)O\(_3\) liquid phase diagram [Tsukihashi]

(Research theme 6): Modeling sinter melting phenomena and bed structure formation [Otomo]

Hitherto, phase diagrams based on Fe\(_3\)O\(_4\)-CaO-SiO\(_2\) and FeO-CaO-SiO\(_2\) systems have been used in sinter melting design. However, attention has been focused on research into compositions with low melting points in raw material conditions where the apparent viscosity increases as mentioned above. In the phase diagram of the Fe\(_2\)O\(_3\)-FeO-CaO system, the melting point is lower at intermediate compositions of FeO and Fe\(_2\)O\(_3\) than at the FeO or Fe\(_2\)O\(_3\) end sides, and therefore we prepared liquidus curves for the CaO-SiO\(_2\) system with iron oxide (Fe\(_3\)O\(_4\)) components at equilibrium with an oxygen partial pressure of 10\(^{-8}\) to 10\(^{-3}\) or thereabouts (corresponding to the sinter reaction process) at
1300°C with added Al₂O₃ components or MgO components (Fig. 13).

According to these results, the liquid phase ratio increases in the vicinity of iron oxide at about 10⁻⁶, suggesting that adding reducing agent or blending in fuel is effective at maintaining a molten state. Also, at both 10⁻³ (start of melting) and 10⁻⁴ (end of melting), it is known that the range of compositions corresponding to the liquid phase region is reduced in size by the addition of an MgO component but expanded by the addition of an Al₂O₃ component, which is significant for keeping mixtures molten over a wide range. Furthermore, with regard to liquid phase ratio in mixtures saturated with iron oxide where CaO/SiO₂ = 1, characteristic effects are exhibited by MgO sources under low oxygen partial pressure conditions. For example, the addition of an MgO component or Al₂O₃ component causes a reduction in the change of liquid phase ratio in an oxygen atmosphere of 10⁻⁶ to 10⁻⁵, and the addition of an MgO component causes the saturated liquid phase ratio of iron oxide at CaO/SiO₂ = 2 to become zero in an oxygen atmosphere of 10⁻⁵. In the future it is hoped that databases will be compiled from information such as wider range of temperature for these systems.

According to model tests relating to the formation of sinters from model raw materials around particle beds consisting of molten material at the outer shell of core particles, it is known that pores in the sintered material are greatly affected by the core/adhering fines ratio, the combined water content in the core particle, the particle size, and the CaO and Al₂O₃ constituents of the outer shell powder. In particular it has been confirmed that combined water content (porosity) of the core particles and the CaO content of the adhering fines have strong effects, and that increasing the proportion of limonite and reducing the slag constituents makes the sintered material more porous, thereby suppressing its contraction and reducing its strength.²⁰ To suppress the porosity of these sintered materials, it is important to suppress the increase in the proportion of solid phase in the melt that accompanies the assimilation of core particles into the melt, and it is necessary to maintain a high density of core particles of about 20%.

It has thus been confirmed that the formation of pores in limonite by thermal decomposition is regulated by the combined water content, and that the melting assimilation rate can also be regulated by this porosity. It has been pointed out that controlling this assimilation rate is an important design parameter in the use of limonite-based ores, and the formation of dense large-diameter granulated materials from Marra Mamba ore is considered to be effective (Fig. 14). The CaO content in the adhering fines is strongly related to the increase of liquid phase ratio in the melt, and in order to maintain this it is thought to be effective to reduce the degree of oxidation of the iron oxide in the melt composition (i.e., increase the FeO content).

3.2.3 Research Results Relating to the Granulation of Marra Mamba Ore

(Research theme 7): Analysis of factors in limonite raw materials that have an effect on granulated materials [Maeda]

(Research theme 8): Development of a raw material granulation simulation model [Kano]

Australian goethite/limonite ore is broadly divided into Marra Mamba ore and pisolithic ore. Pisolithic ore has a coarse size distribution with few particles smaller than 0.125 μm, while Marra Mamba ore is finer with a high proportion of particles measuring 0.125 μm or less, so these ores differ greatly in terms of their particle size. Also, goethite/limonite is generally porous with a high level of water absorbency, and the contact angle between the ore and water is small. Accordingly, to increase the granulated particle size of Marra Mamba ore, it is necessary to increase the moisture content of the raw material. With regard to the contact angle between the ore and water, an ore with a smaller contact angle (i.e., better wetting properties) allows the formation of a finer granulated material with greater strength (Fig. 15). It can be said that this property is exhibited both by the core and the adhering fines that form the granulate, and as the contact angles of ores of the adhering fines and nuclei become smaller, the strength increases, while the strength decreases as the contact angles get larger. Accordingly, limonite is not a bad ore in terms of the fineness of granulated material, although it should be
born in mind that its adhesive forces are slightly inferior to those of Australian hematite ores.

Using the discrete element method (DEM), we analyzed the movement of granulated material particles inside a drum mixer. The rate of growth of the granulate particle size was determined from the balance between adhesive particle growth and particle disintegration. The adhesive growth of particles is related to the rotational movement energy of the particles in the normal direction (per unit particle, per unit time), and the particle disintegration is related to the collision energy between particles in the normal direction (per unit particle, per unit time). As the drum diameter increases, the particle collision energy becomes larger and the granulate size decreases due to breakage, but if the overall rolling motion distances are equal then the rotational movement energy of the particles in the tangential direction becomes equal and the granulate sizes become equal. As the charge ratio of raw material inside the drum increases, the rolling motion conditions become worse and the overall rolling motion distance becomes smaller so that the size of the granulate decreases (Fig. 16). Therefore, in order to produce dense, strong and large granulate mainly using Marra Mamba ore, essential are large drum diameter, long drum length for long traveling distance of granulate, and large amount of water added to raw material.

4. Research Relating to Practical Process Implementations

(Applications WG): Imaging of new processes by applying the achievements of basic research in this research project [Kasai et al.]

4.1. Achievements of Process Image Studies

We had investigated and paid attention to raw material multiple granulation techniques for the production of high quality sinter with high productivity under the conditions of raw materials with a low level of slag constituents and a high proportion of goethite/limonite.

It was pointed out that proper raw material partitioned blending design and close control over the raw material bed structure are required, taking the sintering properties of ores with a high content of combined water into account. By enhancing multiple granulation methods such as separative granulation and selection granulation, we investigated a method for proper placement of the firing induction bed which induces ventilation paths (void network) in the sinter bed and a firing cured bed in which sintering progresses relatively gradually without the need for the occurrence of extreme melting. This process culminated in the development of the MEBIOS (Mosaic Embedding Iron Ore Sintering) method which is illustrated in Fig. 17. This method involves arranging dense pre-granulated pellets (cured layer) in a sinter induction bed with a raw material composition capable of forming a suitable void network under normal sintering conditions. This is done with the aim of forming the cured layer principally from Marra Mamba ore, while forming lumps from the heat supplied to the induction bed and the gas that passes through it. At the same time, it is expected that this method will also play a key role in the formation of a proper void structure by suppressing pronounced flow of the melt in the cured layer.

4.2. Designing High-productivity Sintering Operations

4.2.1. Design of Voids, Pores and Micro-pores

Figure 18 shows the design concept of a porous meso-mosaic texture sinter cake. If the non-solid parts present in the sinter bed are classified into voids, pores and micropores, then the presence of micro-pores is strongly desired in terms of reducibility while the removal of pores is strongly desired in terms of strength and the presence of voids is strongly desired in terms of ventilation properties. These voids, pores and micro-pores are formed by the combination and growth of non-solid parts inside ore particles or between ore particles that are present in or created in the raw material zone. It is thus desirable to suppress the com-
Particulate raw materials with a small particle size have a significant impact on assimilation and growth of micro-pores into pores, and to promote the combination and growth of pores into voids. In sinter processing schemes where fuel is charged inside the particles, voids must be kept in the sinter bed as a prerequisite for maintaining ventilation. Accordingly, even if the combination and growth of pores into voids is promoted, a bed column structure that maintains voids must be maintained at the minimum level. The combination and growth of non-solid parts is governed by the quantity of assimilated melt and the fluidity of the molten parts. The fluidity of the molten parts co-existing in the same liquid are strongly affected by the ratio of solid (liquid) phase, and it is essential to control the melt composition.

4.2.2. Non-uniformity of Sinter Raw Materials and Sinter Beds

Because sintering is a process in which heat is accumulated from top to bottom, differences in heat patterns also exist in the vertical direction of the bed. Accordingly, even with the same raw material state, there are many differences in smelting assimilation and flow conditions inside the sinter bed that accompany differences in vertical position in the bed (heat patterns). If the temperature is increased, the solid phase ratio tends to decrease and the fluid state tends to be promoted.

On the other hand, sinter raw materials are varied widely both in terms of their composition and particle size. Particulate raw materials with a small particle size have a greater degree of surface contact with the melt and are more readily assimilated. Accordingly, as the raw material particle size decreases, the quantity of assimilated melt increases and the melt composition and raw material composition tend to become equal, but conversely as the raw material particle size increases, the quantity of assimilated melt decreases and the melt composition becomes significantly different from the raw material composition.

4.2.3. Assimilation Properties of Limonite

When limonite is subjected to heat treatment, its combined water dissociates, resulting in porous properties with minute pores. These porous ore properties readily promote the assimilation reaction with the sinter melt. The sinter composition has a higher content of iron oxide than the eutectic composition produced in the initial melt, so by uniformly assimilating the ore, the solid phase ratio of the melt increases and the fluidity of the melt decreases. We found that in sinter reactions using hematite ore as the raw material, the initial melt formed from fine-grained components containing CaO and SiO2 is assimilated by melting the nucleating particle ore, while the non-assimilated nucleating particles are left behind. On the other hand, in sinter reactions using limonite ore as the raw material, melting takes place after the initial melt has assimilated porous nucleating particles by permeating into them, so that fragments of ore become suspended in the melt and reduce its fluidity. Thus, as shown in Fig. 19, as the temperature increases, the limonite particles are assimilated more easily than the hematite nucleating particles, but have an adverse effect on the fluidity of the melt. When the temperature is increased until the solid phase has disappeared, the melt becomes highly fluid and is no longer able to maintain voids. So even with the same solid phase ratio, differences in the amount of solid phase present lead to different smelting assimilation behavior and different sintered cake structures.

4.2.4. Designing Sinter Raw Material Beds

By taking the abovementioned characteristics into consideration to obtain an assimilation control method for forming sinter beds with well-developed voids and few pores, we propose a MEBIOS composite granulation loading method in which the raw materials are distributed in the sinter bed in the form of a meso-mosaic. The concept of a practical system is shown in Fig. 20.

According to a study by Otomo,11) the pores produced by thermal decomposition of Marra Mamba are mostly micro-pores measuring 20 μm or less, and the strengthening mentioned in the study by Sasaki et al.10) has little effect. Also, the micro-pores of 10 μm or less reported by Sasaki et al.12) do not readily combine regardless of the melt viscosity or liquid phase ratio, unlike the macro pores, and are retained in the texture of the sinter. On the other hand, according to Tsukihashi et al.’s study,13) increasing the content of CaO or FeO is an effective way of reducing the solid phase ratio of the melt and changing pores into voids. As a bed structure column assuming a blend with a large amount of limonite, Otomo’s study13) showed that there must be at least 20% or so of fine grains that do not assimilate, and that it is important to maintain a solid phase ratio by mixing together fine and rough grain sizes so that thermal cracks do not readily form in order to maintain the solid phase ratio.

In the MEBIOS method, the raw material which is assumed to contain a large proportion of limonite is granulated in two separate blends and a bed of raw material is formed by distributing the two separate raw material beds in the form of a mosaic. One of these is a raw material bed.
that promotes smelting assimilation, which is based on pisolitic limonite and blended with a reducing agent (coke, scale) and CaO. The other is a raw material bed that suppresses smelting assimilation, which is based on Marra Mamba and consists of fine and coarsely granulated material.

4.2.5. Granulation Design of Dense and Coarse Spheres

In order to produce large quantities of dense and coarse granulated material, the selection of raw materials and granulation equipment are very important. To obtain a granulated material with a large particle size, mechanical force must be applied with a large kinetic energy and a long rotational action, and for the raw material properties it is important that the wetting properties, particle size and adhesive forces of the granulated material are able to promote refinement by compressive water removal.

According to an evaluation of limonite granulation properties by Maeda et al.,\textsuperscript{21} Marra Mamba ore lacks adhesive forces, but has many small particles and good wetting properties, and can be evaluated as a brand that facilitates the formation of fine coarse particles. Based on a study of a granulation simulation model by Kano et al.\textsuperscript{22} and Marra Mamba ore granulation tests by Maeda et al.,\textsuperscript{21} it is thought that dense and coarse granulated material can be produced even with a drum mixer. It is thought that the specific equipment operating conditions will need to be quantitatively studied in the future.

4.3. Design of High Quality Sinter

4.3.1. Sinter Composition Designs for Improved High-temperature Properties

According to a study by Nakamoto et al.,\textsuperscript{23} the ventilation properties and reducibility in the high-temperature part (welding zone) inside a blast furnace contribute to the quantity of melt produced and to the permeation blockage state, and it is important to reduce the quantity of melt and alleviate blockages by reducing the permeation forces. The diagram on the left side of Fig. 21 shows the equilibrium liquid regions of the CaO–SiO\textsubscript{2}–FeO system at 1300°C, which represents the slag composition of sinter in a blast furnace in a high-temperature reducing state. The sinter composition in which iron oxide is reduced to FeO (point A) lies in the liquid phase region, while the liquid phase ratio is smaller in a low slag (CaO, SiO\textsubscript{2}) composition (point P) where the high-temperature ventilation properties and reducibility are improved. Furthermore, as mentioned above, the increase of micro-pores in blends with a large limonite content allows the high-temperature reducibility to be further improved. This requires the use of a Marra Mamba ore with a low SiO\textsubscript{2} content rather than a pisolitic ore with a high SiO\textsubscript{2} content.

Next, we will consider applications of the MEBOIS method. The MEBOIS method is characterized in that assimilation between the two separated raw material systems is suppressed. Accordingly, this method results in the formation of sinter textures corresponding to the two separate raw material compositions. In the diagram on the left side of Fig. 21, examples of the two separate conjugate compositions (points P and F) are shown together based on the sinter composition (point A). The sinter composition (point P) lies in a region where solid and liquid coexist, and the solid phase is FeO. If the state of reduction (i.e., the FeO component) is assumed to be constant, then the liquid phase ratio is determined by the CaO/SiO\textsubscript{2} ratio with the lowest liquid phase ratio occurring at CaO/SiO\textsubscript{2} = 1. When the liquid phase ratio is obtained by dividing the conjugation of point P at CaO/SiO\textsubscript{2} = 1 and point F at CaO/SiO\textsubscript{2} = 3, these
points obey the relationship point A > point F > point P, and it is predicted that the liquid phase ratio will be reduced by separating the composition. Thus even when the overall compositions are identical, uneven distribution of the sinters composition can suppress melt formation inside the blast furnace, thereby improving the high-temperature ventilation and reducibility.

4.3.2. Sinter Composition Designs for Improved Reduction Properties

According to the liquid phase diagram produced by Nakazato et al.\(^{17}\) (Fig. 21, right side), reducing the CaO and SiO\(_2\) constituents in the sintered ore results in a smaller liquid phase ratio and lower strength in the sinter production process, but it is thought that the liquid phase ratio can be increased and the strength can be maintained by reducing the oxygen partial pressure. According to a study by Nakazato et al.\(^{29}\) into the mineral texture analysis of sinter with a low oxygen partial pressure (i.e., a high FeO content), silicate slag minerals (2FeO·SiO\(_2\) and FeO·CaO·SiO\(_2\)) produce textures that are very difficult to reduce in the low-temperature reducibility evaluation of mineral textures, and are regarded as textures whose generation should be suppressed. Accordingly, if reducing the oxygen partial pressure and slag content of sinter (i.e., increasing the FeO content and reducing the SiO\(_2\) content) suppresses the formation of slag minerals that are difficult to reduce and increases the Fe\(_2\)O\(_3\) mineral content, then it should effectively improve the strength and reducibility. If it can be assumed that blast furnace slag design is feasible, then according to crystal analysis performed by Sugiyama et al.\(^{91}\) increasing the MgO constituents, Al\(_2\)O\(_3\) constituents and the CaO/SiO\(_2\) ratio should be an effective way of increasing the amount of SiO\(_2\) in solid solution in calcium ferrite minerals with multiple constituents (SFCAM), reducing the levels of silicate slag minerals (2FeO·SiO\(_2\) and FeO·CaO·SiO\(_2\)), and improving the reducibility.

On the other hand, with regard to the reduction degradation properties, it seems that adverse effects are caused by the reduced SiO\(_2\) content and the suspension of hematite minerals that accompany the ease with which limonite is assimilated. However, it is possible to greatly reduce the amount of hematite mineral produced in sinter with a reduced oxygen partial pressure and a high FeO content, and the reduction degradation properties can be improved.

4.3.3. Liquid Phase Ratio in the Sintering Process

From the results of an interrupted firing study by Shigaki et al.\(^{26}\) the partial pressure of oxygen in the sintering process is assumed to reach Fe\(_2\)O\(_3\) equilibrium in the ore surface boundary film, and at the peak sintering temperature state the oxygen partial pressure is in the region of \(10^{-6}\) to \(10^{-4}\). From the equilibrium liquid phase diagram at an oxygen partial pressure of \(10^{-6}\) (Fig. 21, right side), the liquid phase ratios at points P’ and F’ corresponding to the abovementioned points P and F are found to be 50% and 100% respectively, which corresponds to suppression of assimilation of coarse grains and promotion of the assimilation of the powder bed. Furthermore, Tsukihashi et al.’s phase diagram\(^{89}\) suggests that it might be possible to control the liquid phase ratio with the gradient of Al\(_2\)O\(_3\) and MgO. For a coarse granulated material, the addition of MgO to a composition where CaO/SiO\(_2\) = 1 is preferable, but since these are conditions where the liquid phase ratio is small, it is important to use a fine granulated material to facilitate the expression of strength. The above considerations are summarized in Table 1.


In the sintering of a raw material bed with the structure shown in Fig. 17, the first thing that needs to be clarified is the range of proper sizes of the cured layer (preliminary granulation pellets). To avoid uneven firing in the sintering process, it is important that sufficient gas surrounds the bottom of the cured layer, and there ought to be an upper size limit for this purpose. When sintering is expected to take place up to the middle of the cured layer, it is thought that there is also an upper limit on the size from the viewpoint of the heat transfer rate inside the bed. With regard to the former we are performing in-situ observations of the change in the bed void structure with X-ray CT equipment, and with regard to the latter we are in the process of obtaining a quantitative grasp of various refinement phenomena and endothermic/exothermic reactions that take place inside the cured bed, and we are constructing a simulation model.

4.4.1. Observations by X-ray CT

Experiments to observe the change in bed structure were performed using a sinter testing apparatus for X-ray CT observations (sinter bed diameter 100 mm, bed height 100 mm), and model tests in which pre-granulated pellets equivalent to a cured layer are placed in the middle of the sinter bed. Figure 22 shows how the cross-sectional appearance of the sinter bed changes with time when a single 15 mm diameter pellet of (a) a mixture of Marra Mamba ore and coke (4 mass%) and (b) ore L is placed on the sinter bed. In both cases, it can be seen that a gap forms between the pellet surface and the surrounding raw material bed as the firing progresses (directly after passing the front line of firing), and in particular it can be confirmed that a relatively large gap formed underneath the pellet. When the location of the pellet was observed after firing, we observed a texture that looked as if the pellet had disintegrated during firing, together with evidence that firing had progressed by blending the pellet with coke particles.

Accordingly, with regard to the gas flow inside the sinter bed, the distribution of pellets with a diameter of about 15 mm is relatively unlikely to bring about problems associated with highly uneven firing, such as “uneven burning”, and rather with this distribution design it should be possible to preserve the macro-uniformity of firing and control the void network structure. To prevent excess melting and disintegration of pellets due to crack formation during firing, it is important to understand the effects of many different fac-

### Table 1. Design of liquid phase ratio in melt.

<table>
<thead>
<tr>
<th>Block</th>
<th>CaO/SiO(_2) in BF</th>
<th>Sintering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pellet</td>
<td>1.0</td>
<td>30%</td>
</tr>
<tr>
<td>Fine layer</td>
<td>3.0</td>
<td>90%</td>
</tr>
</tbody>
</table>

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tors, such as the blending ratio of constituents such as fine coke breeze and dust containing carbon sources, the CaO concentration, the thermal cracking characteristics of the ore as the temperature increases, the density and blending ratio of pre-granulated pellets, and the blending ratio of coke into the induction bed raw materials. Optimizing the blending conditions based on this information is an important topic for future study.

4.4.2. Simulation Model

On the other hand, with regard to simulation models, we are progressing with the construction and testing of sinter testing using small-scale sinter testing equipment with the aim of acquiring data for fitting the parameter types used in model computations. Figure 23 shows an example of the temporal variation of the pellet surface temperature $T_{C_0}$ and core temperature $T_{C_c}$. Compared with the temperature variation around the pellet, the increase of temperature at the core is delayed, and the peak temperature also tends to be lower. Figure 24 shows an example of the computation region and a mesh constructed in this region. To facilitate comparison with experiments performed using the above-mentioned small-scale sinter testing equipment, the calculations were performed over a cylindrical region obtained by rotating the left edge axis of the mesh, and in principle the calculations were performed in two dimensions. The model took account of the main reactions including the evaporation of moisture from the raw material, the decomposition of limestone, the burning of coke, the generation of calcium ferrite, and the generation and resolidification of melt, and modeled the movement of heat and material. With regard to the gas flow inside the sinter bed, we solved simultaneously for the flow of heat and material by using the rule of thumb expressed by Ergun’s equation to substitute for the pressure loss in the packed bed in the equation of motion. The respective void ratios and typical particle sizes are applied to the induction bed and the firing cured bed. Boundary effects are also taken into consideration in the gas flow in the vicinity of the pellet surfaces. This was done by continuously reducing the value of the void ratio with respect to the prepared calculation mesh from the pellet surface to the average raw material bed.

In the future, we aim to develop a simulation that can be used to ascertain firing conditions and the like for maintaining an adequate thermal history inside the pellets. However, there are still many issues requiring further study, including consideration of the reduction and oxidation reactions that occur in the firing cured bed in cases where coke powder is added to the pellets, for example, and methods for generating meshes for suitably expressing contraction of the bed height or changes in the bed structure caused by the flow of...
Aspect of large sintering method unlike conventional concepts, and it is possible to develop the image of a revolutionary fast, high productivity, and we have made several significant achievements. We have also investigated multiple granulation of raw materials and bed designs as an example of a process image for realizing this aim, and we have devised the MEBIOS method. The basic concept of this MEBIOS method is that it is possible to develop the image of a revolutionary fast, high quality sintering method unlike conventional concepts, and that it is possible to achieve substantial improvements even based on the assumption of using large amounts of goethite/limonite ores of inferior quality. However, as listed below, there are still many topics requiring further study, including clarification of the technical principles and clarification of the basic phenomena involved in processes such as raw material granulation design and raw material bed design relating to the control of sintered cake bed structure:

1. Clarification of technical principles for controlling micro-pores, pores and voids in sintered cake;
2. Clarification of technical principles behind the formation of high strength fired granules with high yield;
3. Clarification of conditions for the efficient production of fine granules;
4. Clarification of conditions for forming high-quality sinter textures; and
5. Development of numerical simulation models for supporting the abovementioned studies.

It is hoped that research into these areas will continue to be promoted.

**REFERENCES**

3) K. Higuchi and R. H. Heerema: *ISIJ Int.*, 45 (2005), 574.

**Table 2.** Green ball pellet of pot test.27)

<table>
<thead>
<tr>
<th>Material</th>
<th>Maramamba 88mass%</th>
<th>BF dust 6mass%</th>
<th>Limestone 6mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>2.9 (dry-g/cm³)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Size</td>
<td>10-15mm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>10 mass%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blend ratio</td>
<td>3:4 mass%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.** Effect of MEBIOS on sintering test.27) (*The same conditions were selected for gas flow rate, charge mass, and blending ratio.)*

<table>
<thead>
<tr>
<th>Item</th>
<th>Ordinary</th>
<th>MEBIOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green pellet</td>
<td>0 mass%</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pellet</td>
<td>1.65(g/cm³)</td>
<td>2.88</td>
</tr>
<tr>
<td>Fine</td>
<td></td>
<td>1.45</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>1.73</td>
</tr>
<tr>
<td>Permeability</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cold</td>
<td>25.3(IPU)</td>
<td>33.2</td>
</tr>
<tr>
<td>Hot</td>
<td>14.2(IPU)</td>
<td>19.1</td>
</tr>
<tr>
<td>Shrinkage</td>
<td>20vol%</td>
<td>8</td>
</tr>
<tr>
<td>Yield</td>
<td>83.0mass%</td>
<td>71.1</td>
</tr>
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