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High Flowability Low Furnace-Pollution Segregation-Free Iron Based Powder Containing No Metallic Soap Lubricant

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A new type of segregation-free iron based powder containing only wax as a lubricant completely and free from metallic soap, CLEAN MIX (KWAX-C), has been developed to improve flowability and productivity in sintering process to lighten the burden in the maintenance of furnace. The flow rate of CLEAN MIX (KWAX-C) is almost equal to that of the conventional segregation-free iron based powder containing wax lubricant, CLEAN MIX (KWAX-A) and the index of flow blocking is smaller by 62%. The powder characteristics; such as compressibility, Rattler value and ejection force of CLEAN MIX (KWAX-C), and the mechanical properties, such as tensile strength, Charpy impact value and dimensional changes during sintering of the compact made of it, were almost equal to those of the conventional segregation-free iron based powder containing wax lubricant.

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1 Introduction

In the field of iron powder metallurgy, high dimensional accuracy in sintered parts is a basic requirement.[1] On the other hand, because powder metallurgy technology must be competitive with other machining methods in productivity and quality, high quality is also required in the raw material powders.

As raw materials used in iron-based sintered materials, alloy powders such as copper powder, nickel powder, graphite powder and lubricants are generally mixed with iron powder, which is the main raw material. However, because the densities of these powders that make up this mixed powder are different significantly, quality deviations of sintered parts may occur due to segregation of the alloy elements during mixing of raw materials and through compacting in the sintered part manufacturing process. Dusting may also be another problem.

To solve such problems, Kawasaki Steel has developed a premixed powder which prevents segregation of graphite powder by fixing the graphite or other alloying element powder to the surface of the iron powder with an organic binder.[2]

Zinc stearate has conventionally been used as the lubricant mixed in segregation-free premixed powder, but the zinc oxide which is formed by the decomposition of zinc stearate during the sintering process adheres to the inside walls of the sintering furnace and causes sooting on the surface of the sintered parts. As a result, manufacturers of sintered products must periodically clean the adhered zinc oxide from the furnace walls, which is a disadvantage at standpoints of both the working environment and the operation efficiency of the sintering furnace. A segregation-free premixed powder that uses a wax type lubricant has been developed to solve this problem. However, by nature, the flowability of this premixed powder is poor. An attempt to improve flowability was to replace part of the lubricant with zinc stearate, but this did not completely solve the above-mentioned problems.

On this background, the development of a segregation-free premixed powder with a wax lubricant that includes no zinc stearate and possesses excellent flowability was desired. In the following, this type of segregation-free premixed powder is called segregation-free premixed powder with 100% wax lubricant.

Ishikawa et al. conducted shearing tests of segregation-free iron premixed powder with wax lubricants, and found that flowability did not depend on internal frictional forces between the particles, but rather depended on the cohesive force between particles.[3] It is known

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that the adhesive force, which is closely related to the cohesive force, consists of the liquid bridge force, electrostatic force, and van der Waals force.4)

In this article, the magnitudes of the liquid bridge force, electrostatic force, and van der Waals force in a commercially available segregation-free premixed powder with wax lubricant is calculated, and the factors that determine flowability are estimated. Adhesive force is experimentally measured and comparison of adhesive force between measured and calculated results is carried out.

Based on this knowledge, the authors developed a segregation-free premixed powder with 100% wax lubricant, "KIP Clean Mix KWAX-C," which has remarkably improved flowability while also possessing powder characteristics and mechanical properties in sintered products equal to those of the conventional segregation-free premixed powder with wax lubricant.

The results of an analysis of the factors that determine the flowability of premixed powder with wax type lubricants and the characteristic properties of the newly developed KIP Clean Mix KWAX-C are also discussed.

2 Experimental Procedure

2.1 Analysis of Factors Determining Flowability of Premixed Powder with Wax Lubricant

Experiments were performed using a commercially available segregation-free premixed powder with wax lubricant (wax lubricant type KIP Clean Mix manufactured by Kawasaki Steel; KWAX-A, composition: Fe-0.8% graphite powder-0.75% lubricant). The adhesiveness for KIP Clean Mix K-WAX-C powder was determined as a ratio of carbon content of the premixes in a diameter range of 75~150 μm to that of the entire premixed powder.1) The shapes of particles, the segregation-free premixed powder, iron powder used, graphite powder, and lubricant were observed by SEM.

The mean particle size of the iron powder was measured using standard sieves, and those of the other kinds of particles were measured by the laser diffraction method.

In order to measure the electrostatic force acting between particles, the charges of a mixed powder of iron powder and 1% lubricant, and that consisting of iron powder and 0.8% graphite powder were measured by the blow off method.5) Because the unit used in measuring the charges was C/g, the specific surface area (m^2/g) of the respective powders was measured by the BET method, then the charges were converted to a unit of C/m^2.

To obtain the humidity range within which the liquid bridge force should be considered, the adsorption isotherm of water vapor on the segregation-free premixed powder with wax lubricant was measured at 25°C.

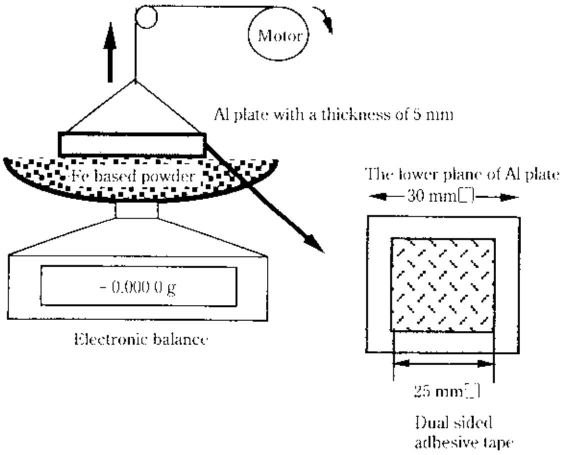

Fig. 1 Schematic description of the system to measure van der Waals force of iron based powders

The van der Waals force of the powder was obtained referring to the method proposed by Fukuzawa.6) As shown in **Fig. 1**, powder was filled into a pan on an electronic balance, and an aluminum plate to which dual-sided adhesive tape had been applied was placed on the powder bed surface from above and then gradually raised in vertical direction. The adhesive force was obtained as the difference between the maximum change in weight and the weight of the particles adhering to the tape. The number of particles adhering to the dual-sided tape was also counted by visual observation with a microscope, and the result was used to calculate the adhesive force per particle.

2.2 Evaluation of Characteristics of KIP Clean Wax KWAX-C

A segregation-free premixed powder with a composition of Fe-2%Cu-0.8%C was prepared using water atomized iron powder (KIP 301A) as the iron powder, and electrolytic copper (mean particle diameter; 32 μm) and natural graphite (mean particle diameter; 24 μm) as simultaneously added elements. Three types of lubricants were used, these being the zinc stearate type, the conventional wax type lubricant (KWAX-A), and the newly developed wax type lubricant (KWAX-C). The amount of lubricant addition was 0.8% in all cases. In order to compare the characteristics of segregation-free premixed powder containing these lubricants, the apparent density, flowability, index of flow blocking (discharge from the hopper), green density at compacting pressures of 392, 490, and 588 MPa.

Rattler value, and ejection force were measured. The index of flow blocking was measured by the following method.

A simple hopper with dimensions of 100 mm × 100 mm × 100 mm and a hole with a diameter of 2.5 mm in the bottom was filled with 1 kg of segregation-free pre-

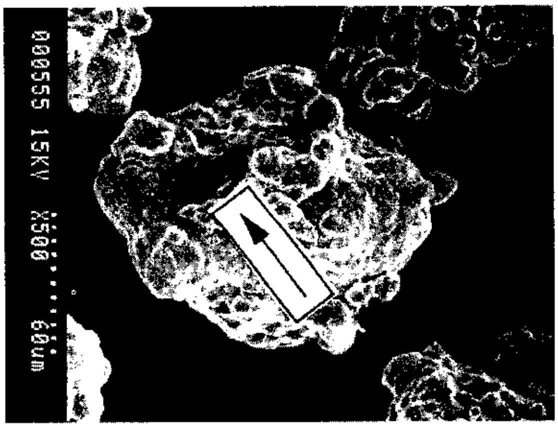

Photo 1 SEM image of the segregation-free iron based powder

mixed powder. Gentle vibration was then applied to the hopper by striking the top surface. The number of striking cycles until the powder discharge started was measured, and the result was used as the index of flow blocking.

To compare the mechanical properties of sintered parts, the respective segregation-free premixed powder were compacted to a green density of 6.85 Mg/m^3 and then sintered at 1 130°C for 20 min in an RX gas atmosphere. After sintering, the tensile strength, Charpy impact value, and dimensional change during sintering relative to the die were measured.

3 Results and Discussion

3.1 Factors Determining Flowability of Iron Premixed Powder with Wax Lubricant

3.1.1 SEM observation of segregation-free iron premixed powder with wax lubricant (KWAX-A)

An SEM image of a segregation-free iron-based premixed powder with wax lubricant is shown in **Photo 1**. The surface of the single iron powder has a roughness on the order of 10 μm. The binder component, which is approximately 20 μm in size, has adhered to a concave part of the powder particle at the position pointed out by the arrow in the photograph. Because the adhesion ratio of the graphite is 80%, it is considered that virtually all the graphite particles have adhered to the surface of the iron powder in a form that is covered with binder. The lubricant was added as a free powder. Based on these SEM observation results, it is considered that the segregation-free premixed powder has a structure of the type shown in **Fig. 2**. The measured results of the mean particle diameter and specific surface area of the powders that make up the segregation-free premixed powder and the Hamaker coefficients used in calculations are listed in **Table 1**.[7] As Hamaker coefficients for the lubricant and binder, the literature value for polystyrene was taken for calculation instead of their measured values because they were not available in the literature.

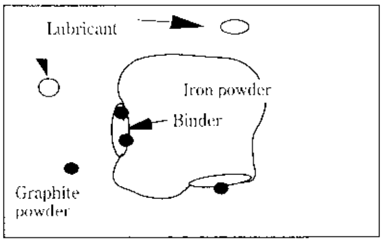

Fig. 2 Illustrative description of the segregation-free iron based powder

Table 1 Hamaker coefficient, mean particle size and specific surface area of iron powder, graphite powder and lubricant powder

Material	Hamaker coefficient (10^{-19} J)	Mean particle size (μm)	Specific surface area (m^2/g)
Iron powder	2.12	80	0.04
Graphite powder	4.70	22	9.18
Lubricant powder	0.70	20	7.50

3.1.2 Calculated results

(1) Liquid Bridge Force

The liquid bridge force is the force attributable to the surface tension due to the adsorbed water film between particles. Assuming the contact angle between the liquid and particle is 0, if the magnitude of the liquid bridge is sufficiently small in comparison with the size of the particle, the liquid bridge force can be expressed by Eq. (1).[8]

$$F_c = -\pi \cdot \gamma \cdot D \cdots\cdots\cdots\cdots (1)$$

Here, γ: surface tension of water (N/m), D; converted particle diameter of two particles (m). The converted particle diameter is given by Eq. (2).

$$D = (D_1 \cdot D_2)/(D_1 + D_2) \cdots\cdots\cdots\cdots (2)$$

Here, D_1, D_2, are the diameters (m) of the respective particles. From Eq. (1), the liquid bridge force is proportional to the particle diameter. Therefore, considering the fact that the iron powder particles are the largest of the particles that comprise the segregation-free premixed powder, the liquid bridge force was calculated based on the iron powder, as the largest liquid bridge force. As a result, the maximum liquid bridge force was calculated to be 1.8×10^{-5} N/particle.

(2) Electrostatic Force

The electrostatic force, which is generated by con-

Table 2 Electrostatic charge measured and electrostatic force calculated

Combination of powder		Charge (μC/g)	Electrostatic force (10^{-12} N/particle)
Iron powder	Graphite powder	0.024	0.42
Iron powder	Lubricant powder	−0.084	2.20

Table 3 Van der Waals force calculated

Combination of powder		van der Waals force (10^{-15} N/particle)
Iron powder	Graphite powder	9.07
Iron powder	Lubricant powder	3.25

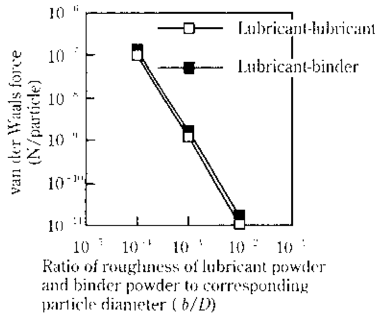

Fig. 3 Effect of roughness of lubricant powder and binder on van der Waals force between lubricants and that between lubricant powder and binder on iron powder

tact among the different kinds component materials of a segregation-free, iron premixed powder, including iron powder, alloy powders, lubricant is shown by Eq. (3).

$$F_e = \pi \cdot \sigma_1 \cdot \sigma_2 \cdot D^2/\varepsilon \cdots\cdots\cdots\cdots\cdots\cdots (3)$$

Where, σ; charge (C/m^2), D; converted particle diameter (m), ε; dielectric coefficient in vacuum (F $\cdot$ m^{-1}). Here, σ_1, σ_2 are the charges of the respective particles. For example, **Table 2** shows that, in a combination of iron powder and graphite powder, the charge of the iron powder is $-0.024\,\mu$C/g, and that of the graphite powder is $+0.024\,\mu$C/g. It should be noted that the charge between the binder and lubricant could not be measured because it was not possible to identify the binder component independently. Table 2 summarizes the actually measured electrostatic charges and the calculated values of the electrostatic force. The electrostatic force was in the range of 10^{-13}~10^{-12} N/particle, irrespective of the type of particle measured.

(3) Van der Waals Force

The van der Waals force comprises a force due to the orientation effect that acts between molecules having a permanent dipole moment and a force that acts when a molecule having a permanent dipole moment polarizes a molecule without the permanent dipole moment. The van der Waals force between two particles is given by Eq. (4).[8]

$$F_{vd} = -A \cdot D/\{24(Z + b)^2\} \cdots\cdots\cdots\cdots\cdots (4)$$

Here, A; Hamaker coefficient (J), Z; distance between particles (40 nm), b; surface roughness of particle (m). The Hamaker coefficient and surface roughness of particles of two different kinds can be expressed by Eqs. (5) and (6), respectively.

$$A = (A_1 \cdot A_2)^{0.5} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (5)$$

$$b = (b_1 + b_2)/2 \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (6)$$

Here, A_1 and A_2 are the Hamaker coefficients of the respective particles, and b_1 and b_2 are the surface roughnesses of the particles. In this work, the van der Waals force was calculated for the two types of particles in various combinations of the metal powders and lubricants that comprise the segregation-free premixed powder.

The results of SEM observation showed that the iron powder consisted of primary particles with diameter range of the order of 10~20 μm, and the magnitude of the surface roughness was approximately 10 μm. The graphite powder was a flat shaped powder with an average diameter of approximately 20 μm. In calculations, the surface roughness of the graphite powder was assumed to be 0 because its surface consisted of cleavage planes that appeared to have been formed during milling. The outer surfaces of the lubricant and binder were smooth. The van der Waals force was calculated for the range where the ratio of the particle surface roughness to the particle diameter, (b/D) was 1.0~0.01%.

Table 3 shows a summary of the van der Waals forces between iron powder and graphite powder and that between iron powder and lubricant powder. The van der Waals force between the iron powder and the two types of particles was on the order of 10^{-15} N/particle. **Figure 3** shows the relationship between the van der Waals forces between the binder and lubricant and between lubricant particles, and the ratio of the surface roughness and the particle diameter. The van der Waals force increases as the smoothness of the surface of the lubricant and/or binder becomes greater, and ranged in magnitude from 10^{-11} to 10^{-7} N/particle. From these calculated results, it is considered that the maximum van der Waals forces are those that act between the binder and lubricant and between lubricant particles.

3.1.3 Forces determining flowability

From the calculated results in section 3.1.2, it was understood that the forces calculated decreases in the order of liquid bridge force > van der Waals force > electrostatic force. The liquid bridge force is considered

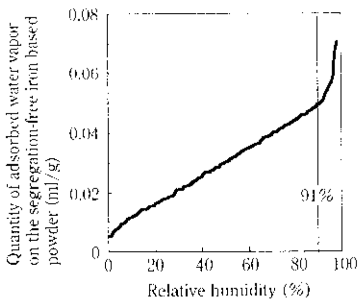

Fig. 4 Adsorption isotherm of water vapor on segregation-free iron based powder used

to occur when water molecules are adsorbed in multiple layers between particles (multimolecule adsorption). **Figure 4** shows the adsorption isotherm of water vapor on segregation-free premixed powder with a wax lubricant. From Fig. 4, it can be said that monolayer adsorption of water molecules occurs up to a relative humidity of 91%, and multimolecule adsorption occurs when the relative humidity exceeds 91%. Based on this result, it is considered possible to ignore the liquid bridge force under the working conditions in which mixing and compacting are performed in ordinary powder metallurgy. Accordingly, the van der Waals force between the binder and lubricant and between lubricant particles is considered to be the main factor determining flowability.

The measured value of the adhesive force in segregation-free premixed powder with a wax lubricant is 10.9 × 10^{-8} N/particle, and thus shows considerably good agreement with the calculated value of the van der Waals force. The adhesive force of zinc stearate lubricant type segregation-free premixed powder, which is superior in flowability to the wax lubricant type, is lower than that of the wax lubricant type, at 3.2 × 10^{-8} N/particle. This is attributed to the fact that, although a constant value was used as the Hamaker coefficient of the lubricant in these calculations regardless of the type of lubricant, in actuality, there are differences in the Hamaker coefficient depending on the type of lubricant.

Based on the results of this study, reducing the van der Waals force between the binder and lubricant and between lubricant particles is considered to be an effective means of improving the flowability of segregation-free premixed powder.

3.2 Characteristics of KIP Clean Mix "KWAX-C"

As discussed above, the most important factor determining flowability is the van der Waals force. Kawasaki Steel therefore developed a new wax lubricant that has low van der Walls force and newly developed the world's first high flowability segregation-free premixed powder with 100% wax lubricant, KIP Clean Mix KWAX-C. The features of this newly developed product are described below.

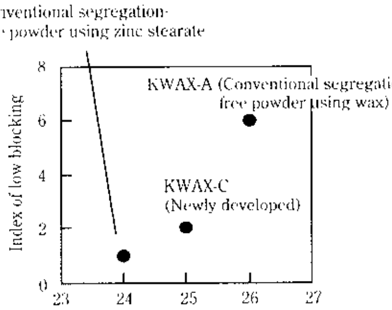

Fig. 5 Flowability of newly developed segregation-free iron powder with wax lubricant

Table 4 Apparent density of segregation-free iron premixed powder

Type of wax	Apparent density (Mg/m^3)
Zinc stearate	3.30
KWAX-A (Conventional)	3.20
KWAX-C (Newly developed)	3.25

3.2.1 Powder characteristics

Figure 5 shows the relationship between the flowability of segregation-free premixed powder and the index of flow blocking. **Table 4** shows the apparent density. The developed product, KIP Clean Mix with wax lubricant, KWAX-C, has virtually the equal flowability to the conventional product, KIP Clean Mix with wax lubricant, KWAX-A. However, the index of flow blocking has been significantly improved in the new product, which shows a value nearly equal to that of zinc stearate lubricant type segregation-free premixed powder. The apparent density of the new product is also substantially the same as that of the conventional wax type product, KWAX-A.

Figure 6 shows the relationship between the compacting pressure and properties of green density, ejection force, and Rattler value. Compressibility, ejection force, and Rattler value for developed product, KWAX-C, are almost equal to those for the zinc stearate type segregation-free premixed powder and the conventional wax type KIP Clean Mix, KWAX-A.

As described above, the newly developed wax type segregation-free premixed powder, KIP Clean Mix KWAX-C, is superior to conventional KIP Clean Mix, KWAX-A, in flowability and the flow blocking index, and shows almost equal compressibility, ejection force, and Rattler values to those of corresponding properties.

3.2.2 Mechanical properties of sintered bodies

Table 5 shows the tensile strength, impact value, and dimensional change during sintering of sintered

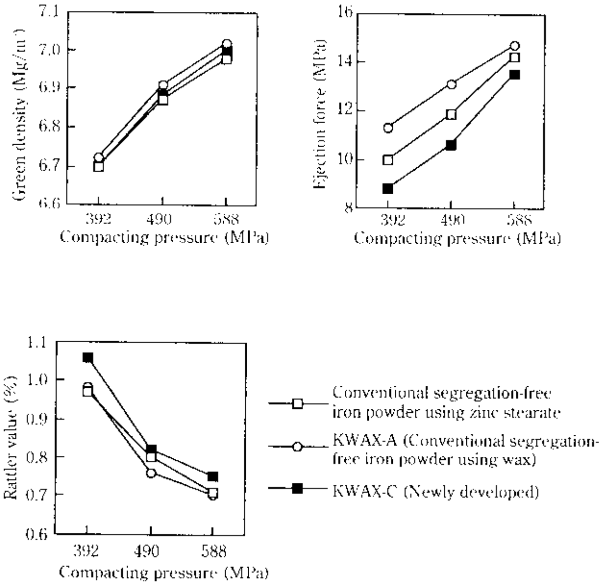

Fig. 6 Green density, ejection force and Rattler value of segregaton-free iron premixed powder

Table 5 Tensile strength and Charpy impact value of sintered body made of the segregation-free iron based powder used and dimentional change during sintering

	Tensile strength (MPa)	Impact value (J)	Dimensional change (%)
Conventional segregation-free premixed powder using zinc stearate	445	10	0.34
KWAX-A (Conventional segregation-free premixed powder using wax)	422	10	0.38
KWAX-C (Newly developed)	434	10	0.40

bodies made using segregation-free premixed powder. The developed product, KWAX-C, shows virtually the equal tensile strength and impact values to those of the zinc stearate type segregation-free premixed powder and the conventional wax type KIP Clean Mix, KWAX-A. The dimensional change during sintering with the developed product, wax type KIP Clean Mix KWAX-C, is also equal to that with the conventional KIP Clean Mix, KWAX-A. The new product shows a slight tendency of approximately 0.06% in comparison with that of zinc stearate type segregation-free premixed powder.

4 Conclusion

(1) The van der Waals forces that act between the binder and lubricant at the iron powder surface and between lubricant particles are concluded to be a determining factor of the flowability of wax type segregation-free premixed powder.

(2) The newly developed segregation-free premixed powder with 100% wax lubricant, KIP Clean Mix KWAX-C, is superior to the conventional product, KIP Clean Mix KWAX-A, in the flow blocking index (index of discharge from the hopper), and shows almost equal compressibility, ejection force, and Rattler values, to those of conventional KIP Clear Mix KWAX-A.

(3) The newly developed KIP Clean Mix with 100% wax lubricant, KWAX-C, shows substantially the equal tensile strength, impact values, and dimensional change during sintering to those of zinc stearate type segregation-free premixed powder and the conventional wax type KIP Clean Mix, KWAX-A.

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