KAWASAKI STEEL TECHNICAL REPORT
No.29 (November 1993)
Special Issue on Iron Power

Segregation-Free KIP CLEAN MIX Powders

Toshiyuki Minegishi, Kiyoshi Makino, Hiroshi Sugihara, Yoshiaki Maeda, Shigeaki Takajo, Ichiro Sakurada

Synopsis :
New mixed powders, KIP CLEAN MIX, were developed to minimize segregation and dusting by a treatment which firmly bonds graphite and other additive powders onto the surface of the iron powder particles. The segregation-free treatment gives a C-adhesion ratio (the ratio of carbon content in 100～200-mesh powder mixtures to carbon content in the total powder mixtures) of more than 80%, while the ratios remained about 20% for conventionally mixed powders. Dusting was also reduced by 90% and flowability was improved by more than 30%. Excessive graphite concentration usually observed in the final stage of feeding from a hopper is completely suppressed by this treatment. Mechanical properties of sintered compacts made from KIP CLEAN MIX powders being very stable, substandard articles were decreased and the yield of sintered parts was improved by about 10%.

The body can be viewed from the next page.

Segregation-Free KIP CLEAN MIX Powders*


Toshiyuki Minegishi
Staff Deputy Manager, Iron Powder & Welding Materials Technology Sec., Iron Powder Dept., Chiba Works


Kiyoshi Makino
Staff Manager, Iron Powder & Welding Materials Technology Sec., Iron Powder Dept., Chiba Works


Hiroshi Sugihara
Iron Powder Control Sec., Technical Control Dept., Chiba Works


Yoshiaki Maeda
Assistant General Manager, Iron Powder Control Sec., Technical Control Dept., Chiba Works


Shigeaki Takajo
Dr. Sci. & Dr. Eng., Senior Researcher, New Materials Research Center, High-Technology Res. Labs.


Ichiro Sakurada
Staff Assistant Manager, New Materials Dept., Chemical Div.

Synopsis:

New mixed powders, KIP CLEAN MIX, were developed to minimize segregation and dusting by a treatment which firmly bonds graphite and other additive powders onto the surface of the iron powder particles. The segregation-free treatment gives a C-adhesion ratio (the ratio of carbon content in 100~200-mesh powder mixtures to carbon content in the total powder mixtures) of more than 80%, while the ratios remained about 20% for conventionally mixed powders. Dusting was also reduced by 90% and flowability was improved by more than 30%. Excessive graphite concentration usually observed in the final stage of feeding from a hopper is completely suppressed by this treatment. Mechanical properties of sintered compacts made from KIP CLEAN MIX powders being very stable, substandard articles were decreased and the yield of sintered parts was improved by about 10%.

1 Introduction

In the field of iron powder metallurgy, the demand for higher strength and precision in sintered parts has been strong in recent years.[1] On the other hand, because powder metallurgy must compete with other processing methods in both the rate of product completion and economy, higher product quality is required in raw materials for powder metallurgy.

The raw material for sintered iron powder parts is typically composed of iron powder as the main raw material, mixed with alloying elements such as copper powder, nickel powder, and/or graphite, and lubricant materials. The various constituent powders of such mixed powders vary greatly in specific gravity and precision, creating problems of dusting and quality variations caused by segregation of the alloying elements in the mixing and compacting processes which are essential to the manufacturing of sintered parts. To solve these problems, Kawasaki Steel began to produce and sell a new mixed powder trade named KIP CLEAN MIX in February 1989. The segregation of graphite and other additive elements, which is a cause of quality variations, is prevented in KIP CLEAN MIX by bonding the additives to the surface of the iron powder particles, which at the same time sharply reduces dusting. KIP CLEAN MIX has won a favorable reputation with users for these advantages.

This paper discusses the powder properties of KIP CLEAN MIX, and describes the features of sintered compacts of this new product in comparison with those produced from conventional mixed powders.

2 Outline of Manufacturing Process for KIP CLEAN MIX

In principle, this new mixed powder is produced by binding graphite and other additive elements firmly to the surface of the iron powder particles using a special binder. When this production process is used, the adhesion ratio of additives shows a decisive increase over the conventional method of simply adding the submaterials to the iron powder and then mixing. KIP CLEAN MIX

* Originally published in *Kawasaki Steel Giho*, 24(1992)4, 262–267

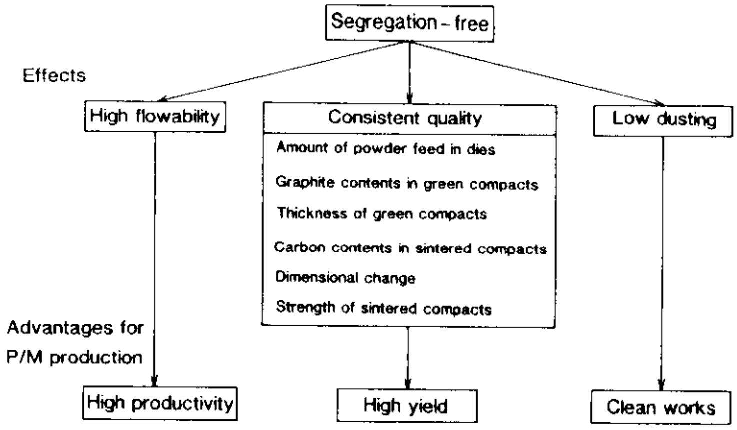

Fig. 1 Characteristics of segregation-free mixed powders

is also superior in compressibility to pre-alloyed steel powders, in which the alloying elements are added to molten steel, and, in comparison with composite steel powders produced by diffusion bonding of alloying elements onto the surface of the iron powder,[2] it offers the advantage of making it possible to apply the elements such as C and Cr, oxides of which are difficult to be reduced.[3]

Because KIP CLEAN MIX powder prevents segregation and dusting, it is expected to make a major contribution to higher productivity and yield, in addition to improving the working environment. **Figure 1** shows the characteristics and advantages of this segregation-free powder.

3 Experimental Method

3.1 Definition of C-Adhesion Ratio

In advance of the experiments, a "C-adhesion ratio" was proposed as an index of the uniformity of adhesion of the additive elements in mixed powder to the surface of the iron powder particles, and simultaneously, of powder segregation. The C-adhesion ratio is defined in Eq. (1).

C adhesion ratio (%)

$$= \frac{[C]}{[C']} \times 100$$

$$= \frac{[C]}{[Gr] + 0.68 \times [Zn\ St.] + X \times [B]} \times 100 \cdots (1)$$

[C]: Carbon content in powder mixture between 100 and 200 mesh
[C′]: Carbon content in total powder mixture
[Gr]: Mixed amount of graphite
[Zn St.]: Mixed amount of zinc stearate
[B]: Mixed amount of binder
X: Weight fraction of carbon in binder

Because the additive graphite is extremely fine-grained, conventional mixed powders show virtually no C content in the coarse particle diameter region of +200 mesh (+75 μm). However, a considerable C content is found in this particle diameter region when graphite is bonded to the surface of the iron powder particles using the new treatment to prevent segregation. To make a clear evaluation of the degree of adhesion, the mixed powder is sieved with a 100/200 mesh (75/150 μm) for 5 min with a vibrating sieve. The C-adhesion ratio is then evaluated as the ratio of the C value in this particle size range to the C value in the total powder mixture.

3.2 Experimental Conditions

A comparative test of KIP CLEAN MIX and conventional mixed powders was made using water-atomized iron powder (KIP 300A). As additive elements, electrolytic copper powder (average particle diameter, 48 μm), natural graphite powder (average particle diameter, 20 μm), and zinc stearate were mixed simultaneously with the iron powder. In KIP CLEAN MIX, a special organic material was also used as a binder in the segregation prevention treatment. Two test compositions were selected, Fe-2.0%Cu-1.0%C and Fe-2.0%C. With each of these compositions, two types of segregation-free powder with differing C-adhesion ratios were prepared.

A direct type dust meter of a type commonly used in environmental measurements was employed to measure dust generation from the mixed powders.

The mixed powder characteristics measured were apparent density, flowability (flow rate), green density at a compacting pressure of 588 MPa, Rattler value, and ejection force. In comparing the features of the sintered compacts, hardness, tensile strength, the Charpy impact value, and dimensional change were evaluated. The degree of segregation was evaluated in terms of dimensional change during sintering and variations in combined carbon content. In these experiments, mixed powder fed from the double step hopper shown in **Fig.**

2 was sampled, compacted and sintered, a uniform 6.8 Mg/m^3 was applied as the compacting condition, and sintering was conducted at 1 130°C for 20 min in an endothermic gas atmosphere (CO_2 = 0.3%).

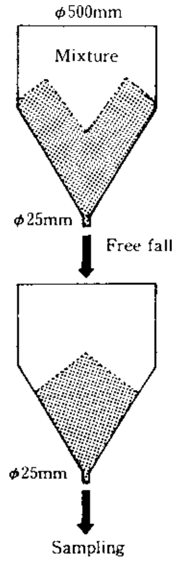

Fig. 2 Schematic diagram of the double step hopper

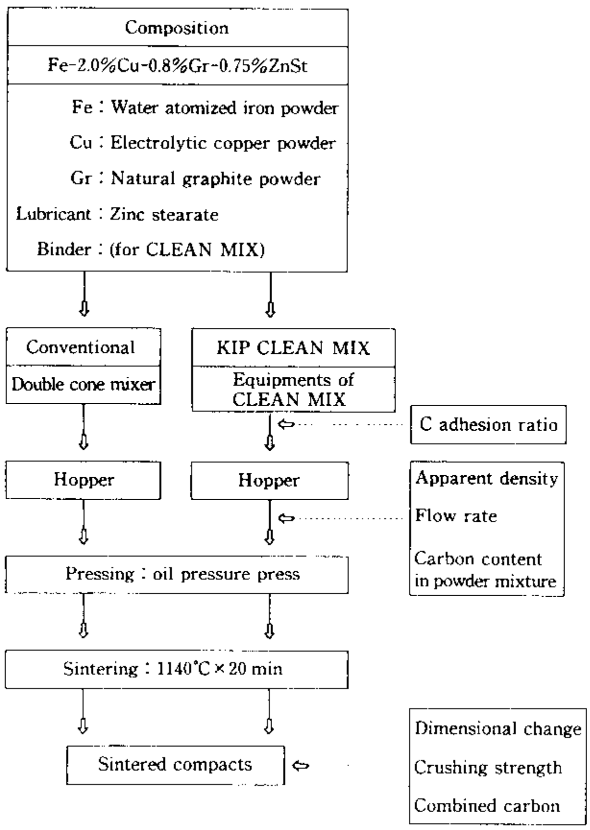

Fig. 3 Flow chart of experimental procedure

To confirm the superiority of KIP CLEAN MIX, changes in the apparent density, flowability, and C content from the hopper to continuous discharge were compared against those with conventional mixed powders, simultaneously with the trend in the characteristics of continuously compacted and sintered pieces made under customers' actual use conditions. The flow of this experiment is shown in **Fig. 3**.

3.3 Effect of Additives

Finally, the effect on properties of the additives used with KIP CLEAN MIX was examined. First, because the additive graphite has most pronounced effect on dimensional changes, the particle diameter of the graphite powder was varied in the range of 6 μm to 34 μm (volumetric average particle diameter) in order to determine the effect of this parameter on dimensional changes. Next, because the type of lubricant has a major influence on powder properties, the effect of dry and wet type zinc stearates and amide waxes was investigated.

4 Experimental Results and Comments

4.1 Results of Measurement of C-Adhesion Ratio and Dust Generation

The C-adhesion ratios of KIP CLEAN MIX and the conventional mixed powders are shown in **Fig. 4**. In comparison with the 20% C-adhesion ratio of the conventional mixed powder, KIP CLEAN MIX showed a value of over 80% in both the Fe-2.0%Cu-1%C and Fe-2%C compositions, indicating that the additive graphite in the new mixed powder strongly adheres to the particle surface of the iron powder.

The results of a measurement of dusting made with the Fe-2.0% Cu-1% C composition are shown in **Fig. 5**. A suppressed-segregation powder with a C-adhesion ratio of 51% showed little improvement in dust preven-

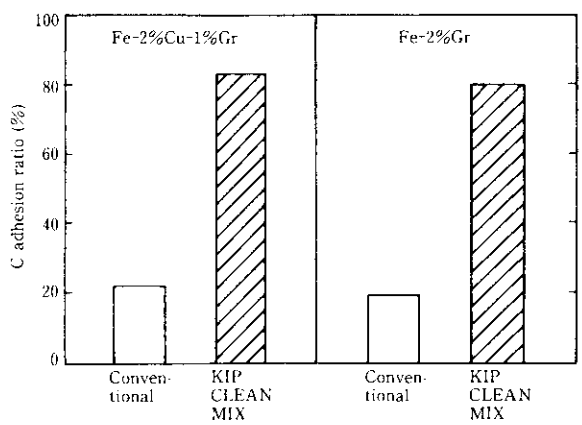

Fig. 4 Adhesion ratio of graphite in powder mixtures

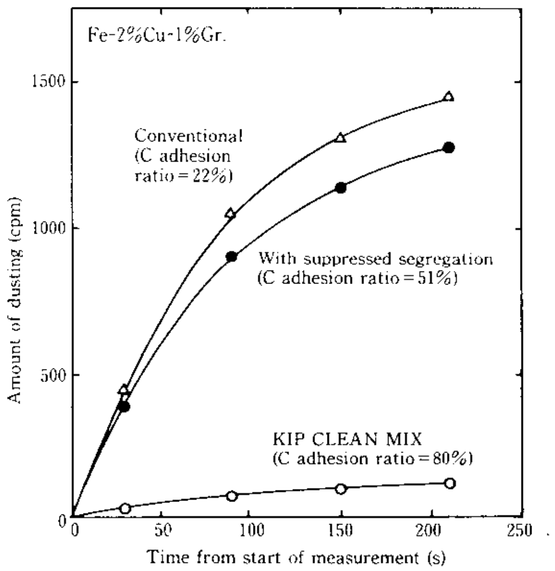

Fig. 5 Dusting of powder mixtures

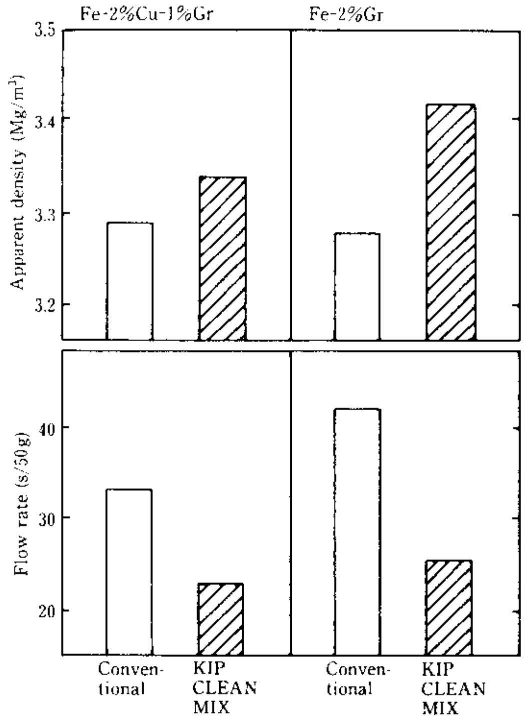

Fig. 6 Apparent density and flow rate of powder mixtures

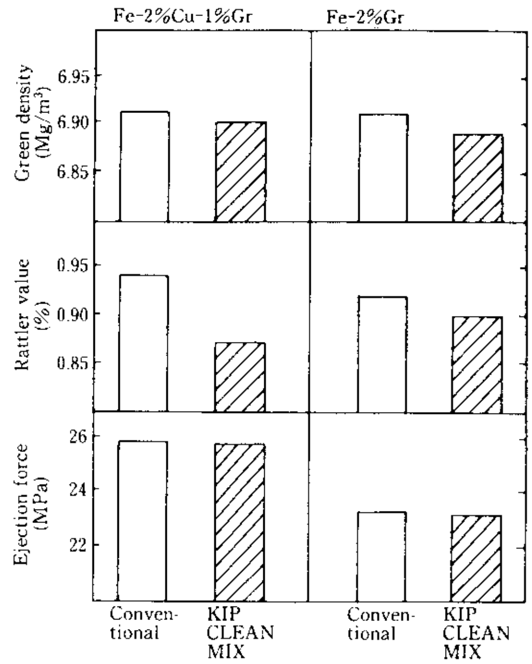

Fig. 7 Green density, Rattler value and ejection force of powder compacts (compacted at 588 MPa)

tion over that with the conventional powder, with a C-adhesion ratio of 22%. However, when the adhesion ratio reached 80% with KIP CLEAN MIX, the amount of dusting dropped dramatically, to less than 10% of that with the conventional powder.

4.2 Characteristics of Powders and Green Compacts

The measured results of the apparent density and flow rate of KIP CLEAN MIX and the conventional powders are shown in **Fig. 6**. In both compositions, the apparent density of KIP CLEAN MIX was higher than that of the conventional powders, and the flow rate was faster, showing an improvement of approximately 30%. The increase in apparent density and improvement in flow rate were achieved as a result of the firm bonding of fine additive elements to the particle surface of the iron powder, and give the mixed powder good filling performance in the die.

The measured green density, Rattler value, and ejection force of KIP CLEAN MIX and the conventional powders are shown in **Fig. 7**. In both compositions, KIP CLEAN MIX showed green density and Rattler values similar to those of the conventional mixed powders, while the Rattler value showed better, i.e. somewhat lower values. The reason for the changes in these characteristics was considered to be the uniform distribution of additive elements in the green compact.

Because a special binder is used with KIP CLEAN MIX, an investigation was made of changes in the characteristics of the product over time after manufacture, with the results shown in **Fig. 8**. The apparent density, flowability, green density, ejection force, and C-adhesion ratio of KIP CLEAN MIX were all extremely stable, showing virtually no change during an eight week period after production.

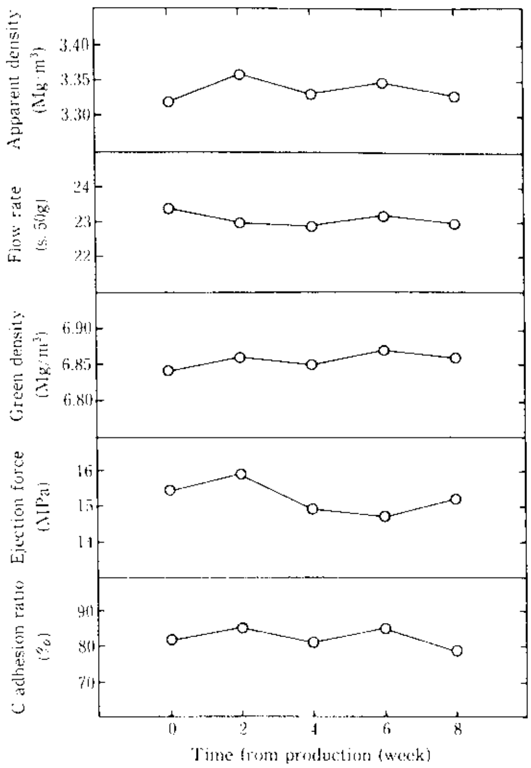

Fig. 8 Characteristics after storage (Fe-2%Cu-1%Gr, compacted at 490 MPa)

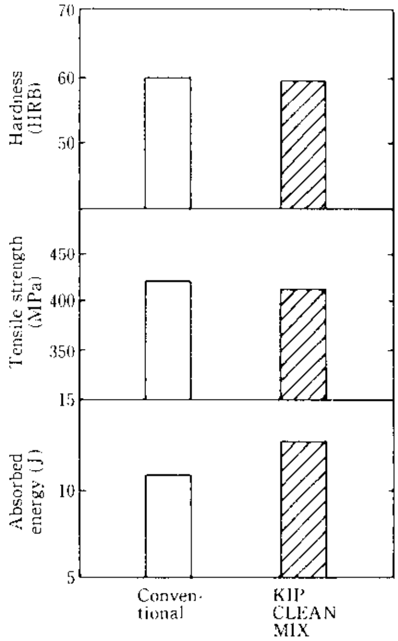

Fig. 9 Hardness, tensile strength and unnotched Charpy adsorped energy of sintered compacts (Fe-2%Cu-1%Gr, green density 6.8 Mg/m^3).

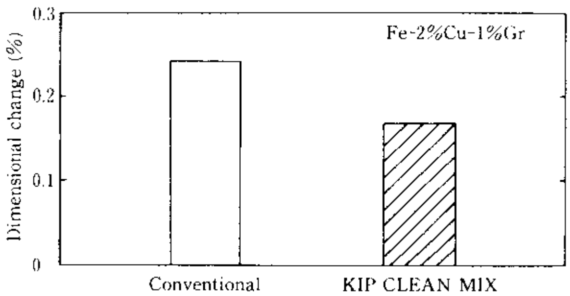

Fig. 10 Dimensional change during sintering (die basis, green density 6.8 Mg/m^3)

4.3 Characteristics of Sintered Compacts

The measured hardness, tensile strength, and Charpy impact values of sintered compacts of KIP CLEAN MIX and conventional powders are shown in **Fig. 9**. Sintered compacts of KIP CLEAN MIX showed substantially the same values for hardness and tensile strength as those of the conventional powders, and excellent, significantly higher Charpy impact values. This was attributed to the fact that, because graphite adheres uniformly to the surface of the iron powder particles in KIP CLEAN MIX, the graphite is uniformly diffused through the iron powder, and as a result it is possible to obtain a uniform structure in the sintered compacts.

Similarly, dimensional change during sintering is shown in **Fig. 10**. Dimensional change with KIP CLEAN MIX was significantly smaller than with the conventional powders. This was considered to be a result of the fact that Cu diffusion to the iron atoms was suppressed and hence what is termed Cu expansion was controlled by better diffusion of C among the iron atoms during sintering, which in turn was due to the more uniform distribution of C with KIP CLEAN MIX.[4,5]

4.4 Effect on Segregation during Feeding from Hopper

Figure 11 shows dimensional change during sintering using a mixed powder of the Fe-2.0%Cu-1%Gr composition discharged from a two step hopper, together with the combined carbon content of the sintered compacts. With the conventional mixed powder, excessive segregation was observed in the final stage of feeding (from about 140 kg onward), and the value of dimensional change fluctuated sharply. Little improvement was seen in either excess C segregation or instability of dimensional change with the mixed powder treated to suppress segregation (C-adhesion ratio, 51%), but with KIP CLEAN MIX (C-adhesion ratio, 80%), C segregation in the final stage of feeding was completely eliminated and dimensional change was stable.

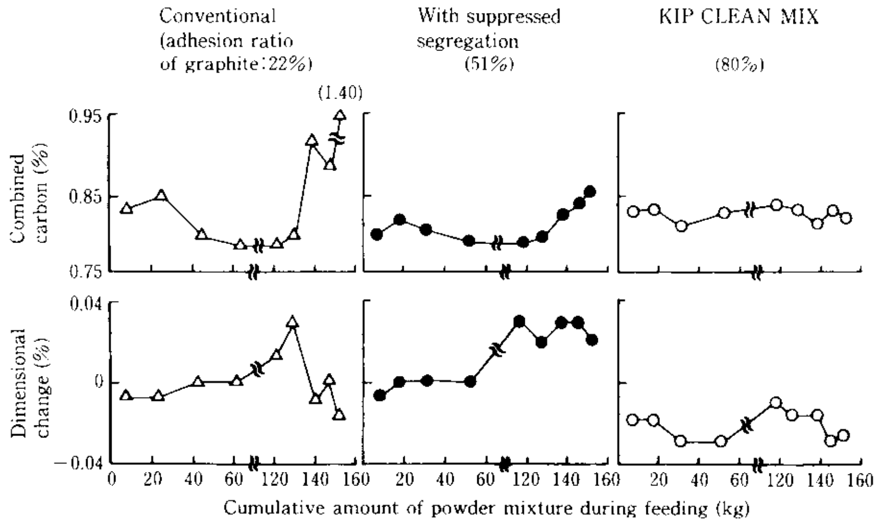

Fig. 11 Variation in dimensional change (powder compact basis) during sintering and combined carbon after sintering for Fe-2%Cu-1%Gr powder mixtures fed from a hopper with periodical sampling

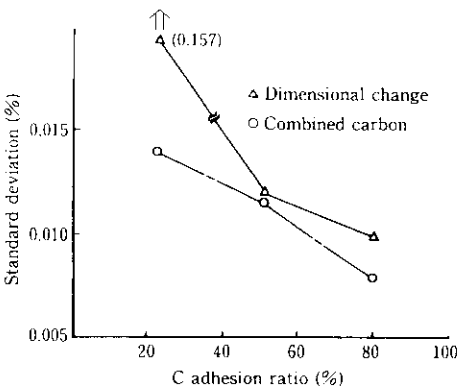

Fig. 12 Influence of C adhesion ratio on standard deviations of dimensional change during sintering and of combined carbon after sintering (Fe-2%Cu-1%Gr)

Figure 12 shows the relationship between the C-adhesion ratio and deviations in combined carbon after sintering on the one hand, and dimensional change on the other. When the C-adhesion ratio increased from 22% to 80%, variations in combined carbon after sintering decreased by 50% (standard deviation, 0.014 → 0.007), while variations in dimensional change dropped by 90% (standard deviation, 0.157 → 0.016). In other words, if the C-adhesion ratio is increased, deviations attributable to mixed powder segregation during the material-feeding process can be dramatically improved.

To further confirm the outstanding characteristics of KIP CLEAN MIX, trends in the apparent density, flow rate, and C content of mixed powders were measured when a total of 1 000 kg of powder was fed from a hopper under actual use methods, as shown in **Fig. 13**. KIP

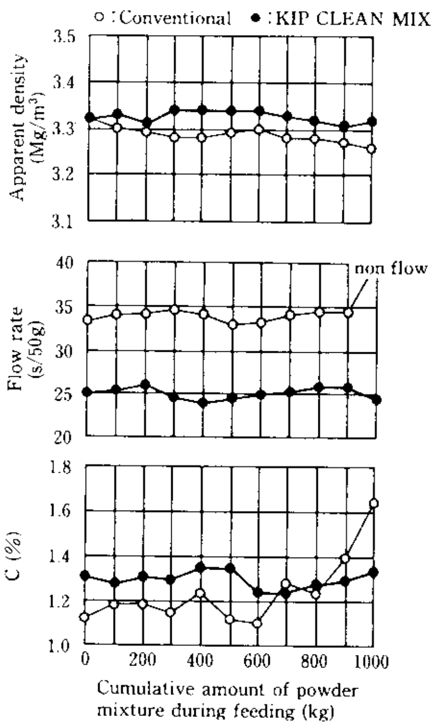

Fig. 13 Variation in properties for powder mixtures fed from a hopper with periodical sampling

CLEAN MIX showed consistently stable values for all characteristics from the beginning of feeding to the end. In contrast, the conventional powder showed a gradual deterioration in apparent density as the cumulative feed amount increased, and the flow rate fell to a zero (unmeasurable) level before the end of the test. The trend in C content clearly suggests that the cause of this problem with the conventinal powder was progressively

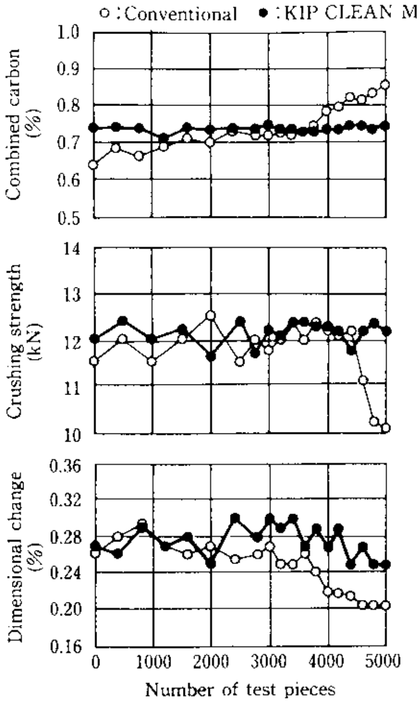

Fig. 14 Variation in crushing strength, combined carbon and dimensional change of sintered compacts

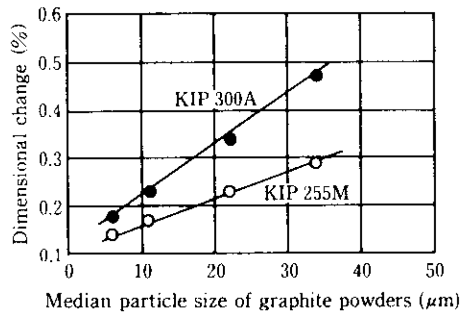

Fig. 15 Effect of average particle diameter of graphite powder on dimensional change of sintered compacts

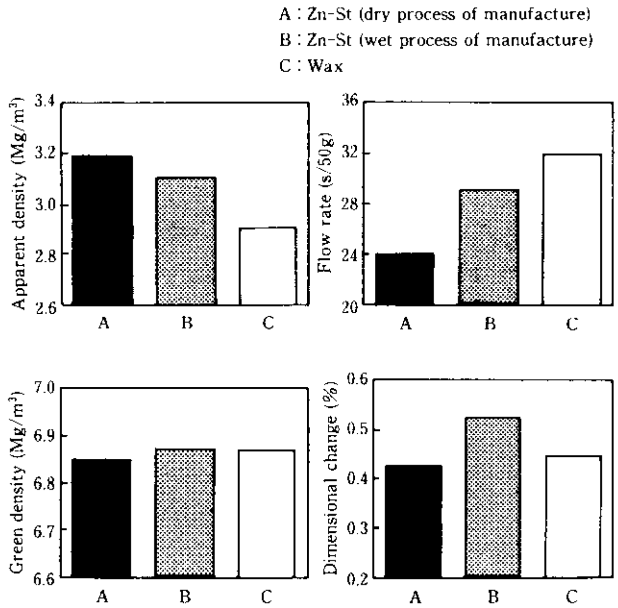

Fig. 16 Effect of lubricant on properties of powder mixtures

greater segregation of the graphite in the hopper as feeding continued.

Figure 14 shows the trend in the crushing strength, combined carbon content, and dimensional changes of sintered compacts when 5 000 pieces were continuously compacted under the conditions typically applied with mixed powders in mass production. With the conventional mixed powder, the previously discussed problem of graphite powder segregation affected the properties of the sintered compacts. As the number of compacted pieces increased, the combined carbon content of the sintered compacts gradually increased, resulting in a progressive contraction in dimensional change. In particular, the products after No. 4500, corresponding to the final stage of powder feeding, show a sharp drop in crushing strength, which was attributed to the fact that the higher graphite content brought about by segregation causes cementite to precipitate in the structure of the sintered compacts.[6] Products of this type are out of standard and represent a yield loss of approximately 10%. In marked contrast, with KIP CLEAN MIX, all characteristics are stable and show no relationship to the order of compacting. It is therefore possible to continue to produce products of consistent quality until the supply of powder in the hopper has been exhausted.

4.5 Effects of Additives

Figure 15 shows the results of an examination of the effect on dimensional change of the volumetric average particle diameter of the graphite powder used in KIP CLEAN MIX. As is clear from this figure, dimensional change decreases when the average particle diameter of the graphite is smaller. This is attributed to suppression of Cu growth as finer-grained graphite powders with a smaller average particle diameter tend to promote a stronger reaction with the iron powder.[7] Moreover, it is also possible to control dimensional change in sintered compacts by adjusting the average particle diameter of the graphite powder.

The effect of the lubricants used with KIP CLEAN MIX was investigated, with the results shown in **Fig. 16**. Recent years have seen a continuing increase in the use of wax, which, unlike zinc stearate, does not include zinc. However, when wax is used, the apparent density of the mixed powder decreases and the flow rate is retarded. Although the reasons for these problems are still unclear, an elucidation of the cause and quick improvement are needed.

5 Conclusions

Newly developed KIP CLEAN MIX powder features a segregation-preventive treatment in which graphite powder and other additive elements are firmly bonded to the surface of the iron powder. The results of development are summarized below.

(1) To evaluate the degree of powder segregation, the C-adhesion ratio was defined as the ratio of the content of 10-200 mesh carbon in the iron powder to the C content of the total powder mixture.

(2) Powders with compositions of Fe-2.0%Cu-1.0%C and Fe-2.0%C showed a C-adhesion ratio of over 80%, in contrast to the 20% value of conventional mixed powders. Thus, flowability has been remarkably improved in the new product.

(3) The characteristics of green compacts and sintered compacts of KIP CLEAN MIX also showed values equal to or better than those of the conventional mixed powders. Moreover, these excellent properties showed no deterioration during long term storage.

(4) The segregation-preventive treatment completely eliminates C segregation in the last stage of feeding from the hopper, contributing to the stability of dimensional change and mechanical strength in sintered parts manufactured from KIP CLEAN MIX.

(5) The use of segregation-free KIP CLEAN MIX powder not only results in an improved environment by preventing dusting, but also makes it possible to increase productivity in the manufacture of sintered parts and achieve an increase in product yield of approximately 10%.

References

1) Y. Morioka and S. Takajo: "Recent Developments in Low-Alloyed Steel Powders," Modern Developments in Powder Metallurgy, Vol. 21, Proc. the 1988 Intl. Powder Metal. Conf., (1988), 521
2) K. Ogura, T. Abe, Y. Morioka, T. Minegishi, E. Hatsugai, and S. Takajo: "Characteristics of Composite-type Alloy Steel Powders Containing Ni, Cu and Mo," '87 Intl. Symp. & Exh. on Sci, and Tech. Sintering, (1987), 148
3) P. F. Lindskog and G. F. Boccini: "Development of High Strength P/M Precision Components in Europe", *Intl. J. Powder Metal. & Powder Tech.*, **15**(1979)13, 199
4) K. Majima and H. Mitani: *J. Jpn. Inst. Met.*, **40**(1976)4, 327
5) H. Kuroki and S. Fujisawa: The Proceedings of the 1988 Autumn Conf., (1988), 138, [JSPPM]
6) N. Goto: Case Studies of Production Efficiency Improvement No. 11, (1990), 15, [JPMA]
7) A. Griffo and R. M. German: "Powder Selection and Sintering Pathways for Zero Dimensional Change in Fe-2Cu-0.8C," Powder Metallurgy World Congress, (1992)