KAWASAKI STEEL TECHNICAL REPORT
No.16 (June 1987)

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Kawasaki steel began to produce alloyed steel powders, ***KIP 4100V*** *and* ***KIP 4100VS****, which are equivalent to AISI 4100. New facilities were constructed in Chiba Works in 1985. They consist of wateratomization and vacuum annealing processes for manufacturing alloyed steel powders. Generally, it is difficult to deoxidize Mn-Cr alloyed steel powders by the gas reduction method. But we succeeded in producing alloyed steel powders with low O, C and N contents (0.10% O, 0.02% C, 0.001% N) by a newly developed process named VALCON (Vacuum annealing process for alloyed steel powders with low carbon, oxygen and nitrogen). These powders obtained by this method are better in compressibility and compactibility (green density of 7.14 g/cm^3, and Rattler value of 0.44% at compating pressure of 7 t/cm^2), especially possessing the advantage of high strength after heat treatment. These features are suitable for high strength sintered parts for heat and wear-resistance.*

1 Introduction

Demand for iron-based sintered machine parts has grown in recent years, with use centered, in particular, in the automotive industry. High strength parts are increasingly being manufactured by sintering, as a result of the imperative to reduce both the weight and cost of automobiles. Since the physical properties of sintered parts vary with the characteristics of powder materials, materials themselves have also assumed great importance.

For conventional parts with relatively low strength and toughness requirements, mixing powders, principally pure iron powder, have been adequate. However, for high strength and toughness parts produced by sintering, a reexamination of alloyed steel powders has be come essential. Alloyed steel powder is produced mainly by the atomization process, in which molten steel is pulverized by a pressurized fluid. Generally speaking, low-value alloyed steel powders can be advantageously manufactured by water-atomization, with low-priced Mn and Cr as alloy elements. However, if Mn- or Cr-alloyed steel powder is manufactured through the conventional water-atomization gas-reduction process, it is rather difficult to reduce the oxygen content in the steel powder due to the strong affinity of oxygen for these elements. For this reason, it has been impossible to improve compressibility, to increase the powder density, and hence to make high strength sintered parts.

An attempt was made, therefore, to develop a method of manufacturing steel powder of low oxygen content, using vacuum annealing as a method of deoxidizing Mn- or Cr-steel containing powders. Based on this method, vacuum annealing facilities with a capacity of

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100 t/month have been installed at Chiba Works, and manufacturing and marketing have begun.

This report describes the principle of vacuum annealing and presents an outline of the vacuum annealing process and the properties of powders produced by this process. These products, corresponding to AISI 4100, are **KIP 4100 V**, **KIP 4100 VS**, and a Cr-Mo-V alloyed steel powder, **KIP 30 CRV**. (Kawasaki Steel's alloyed steel powder products are designated as follows: Mn-Cr-Mo alloy, KIP 4100; Cr-Mo-V alloy, KIP 30 CRA; and those produced by the vacuum annealing process, KIP 4100 V, KIP 4100 VS, or KIP 30 CRV, with the letter V added. KIP 4100 VS, with the letter S added, is a version of KIP 4100 V with improved compressibility.)

2 Outline of Vacuum Annealing Process

2.1 Problems in Gas Reduction Process

Previously, Mn- or Cr-including alloyed steel powders were produced at kawasaki Steel through the water-atomization gas reduction process, but this process involves various problems. In order to use gas reduction to reduce oxides of Mn and Cr produced in the water-atomization process, an atmosphere with a low dew point is required. For instance, when reducing Cr_2O_3 with pure hydrogen, the $RT\ \ell n\ P_{O_2}$-temperature diagram[1)] requires $P_{H_2}/P_{H_2O} > 10^4$ at 1000°C. A large amount of gas must be consumed to maintain a low dew point in the furnace; this, of course, is highly disadvantageous economically.

On the other hand, to obtain low-carbon steel powder, decarburization at a raised dew point is required. However, a reducing atmosphere with high dew point is not compatible with high purity, making it very difficult to realize reduction and decarburization at once. Moreover, as Cr has a strong affinity with nitrogen, a low-nitrogen atmosphere is required. These considerations indicate the number of problems inherent in realizing an industrial gas reduction process.

2.2 Mechanism of Reducing Cr_2O_3 under Vacuum

When heating as-atomized Cr-C-alloyed steel powder, reactions represented by Eqs. (1) through (4) take place. Each of these reactions releases CO gas, increasing the pressure within the reaction vessel. The evacuation of CO gas will accelerate these reactions. While Eqs. (1) to (4) concern Cr, similar reactions apply to Mn.

$$13C + 3Cr_2O_3 \longrightarrow 2Cr_3C_2 + 9CO(g) \cdots\cdots\cdots (1)$$

$$27Cr_3C_2 + 5Cr_2O_3 \longrightarrow 13Cr_7C_3 + 15CO(g) \cdots (2)$$

$$3Cr_7C_3 + Cr_2O_3 \longrightarrow Cr_{23}C_6 + 3CO(g) \cdots\cdots\cdots (3)$$

$$Cr_{23}C_6 + 2Cr_2O_3 \longrightarrow 27Cr + 6CO(g) \cdots\cdots\cdots (4)$$

A schematic diagram of the process of reduction under vacuum is shown in **Fig. 1**. When heated, the C in powder particles diffuses out to reduce Cr_2O_3 at the surface. The resultant CO gas is released from the particle surface.

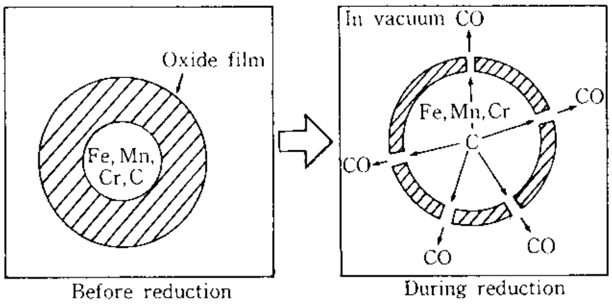

Fig. 1 Schematic illustration of reduction process in vacuum

The progress of the reduction process as it depends upon the reaction gas pressure will now be explained in the thermodynamic terms: The equilibrium oxygen partial pressure of $CO\text{-}CO_2$ mixed gas of total pressure $P(P_{CO} + P_{CO_2})$, equilibrated with a Fe-C system of fixed carbon content, is represented in Eq. (5), using the activity of carbon in iron, a_C, and total pressure P.

$$K_2(\sqrt{P_{O_2}})^2 + K_1\sqrt{P_{O_2}} - \frac{P}{a_C} = 0 \cdots\cdots\cdots (5)$$

where K_1 and K_2 are equilibrium constants of reaction as given in Eqs. (6) and (7).

$$C + \frac{1}{2}O_2 \rightleftarrows CO \cdots\cdots\cdots\cdots\cdots\cdots (6)$$

$$C + O_2 \rightleftarrows CO_2 \cdots\cdots\cdots\cdots\cdots\cdots\cdots (7)$$

$$K_1 = \frac{P_{CO}}{a_C P_{O_2}^{1/2}} \cdots\cdots\cdots\cdots\cdots\cdots\cdots (8)$$

$$K_2 = \frac{P_{CO_2}}{a_C P_{O_2}} \cdots\cdots\cdots\cdots\cdots\cdots\cdots (9)$$

From Eq. (5), it is evident that, as total pressure P is reduced, the equilibrium oxygen partial pressure P_{O_2} of the $CO\text{-}CO_2$ mixed gas is lowered, under conditions of fixed temperature and carbon activity, making it easier to reduce oxide which is otherwise more difficult to reduce.

On the other hand, it has been reported that Cr-alloyed steel powder is denitrified at 1000°C or higher in vacuum sintering.[2)] Since the equilibrium solubility of nitrogen in molten steel is believed to follow Sieverts' law[3)], as represented by Eq. (10), the evacuated atmosphere in the vacuum annealing process is advantageous for reducing the equilibrium nitrogen solubility of alloyed steel powder, and hence for denitrification.

$$[\%N] = K'\sqrt{P_{N_2}} \cdots\cdots\cdots\cdots\cdots\cdots\cdots (10)$$

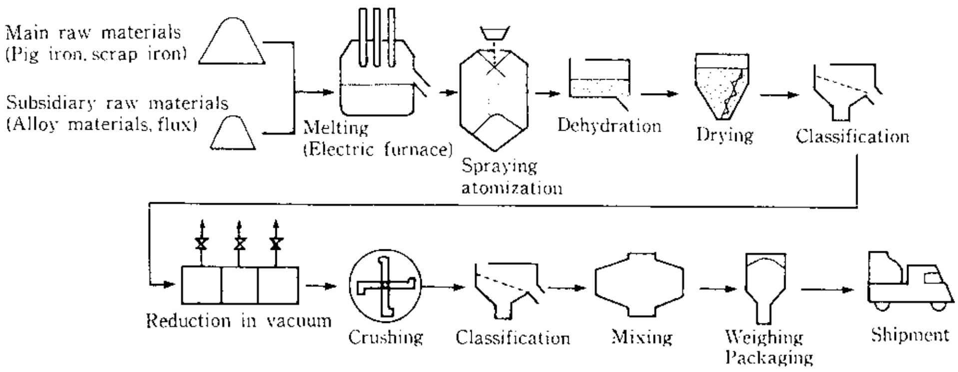

Fig. 2 Manufacturing process of KIP 4100 V

3 Manufacturing Process

An outline of the manufacturing process is shown in **Fig. 2**. The process consists of atomizing and finishing. The alloyed steel powder used is produced on an single-purpose line designed to avoid contamination by pure iron powder.

In the atomizing process, high purity scrap produced at the Chiba Works is used as raw material, and alloyed with Mn, Cr, and C in a 5-t steelmaking arc furnace. Molten steel is atomized by water-atomization$^{4)}$ using a pencil jet developed by Kawasaki Steel and converted to as-atomized powder through dehydration, drying, and classification.

In the reduction process, the as-atomized poweder materials are reduced in the vaccum annealing furnace, and then, through crushing, classifying and mixing processes, powder products are produced. The vacuum annealing furnace used is a three room type, as shown in **Photo 1**.

4 Characteristics of Steel Powder

4.1 Properties of Steel Powder

The chemical composition and physical properties of Mn-Cr-Mo alloyed powders KIP 4100 V and KIP 4100 VS as well as Cr-Mo-V alloyed KIP 30 CRV, manufactured through the vacuum annealing method, are shown in **Tables 1**, **2**, and **3** and the green density and Rattler value in **Figs. 3** and **4**, respectively. For purposes of comparison, characteristics of KIP 4100 and KIP 30 CRA alloyed steel powder manufactured through the gas reduction method and KIP 300 A atomized pure iron powder are also shown.

As shown in Table 1, the content of oxygen $\underline{O}$ is clearly reduced in KIP 4100 V, KIP 4100 VS, and KIP 30 CRV in comparison to that in the conventional products. Particularly, $\underline{O} = 0.10\%$ for KIP 4100 VS and $\underline{O} = 0.12\%$ for KIP 30 CRV are much lower than the value

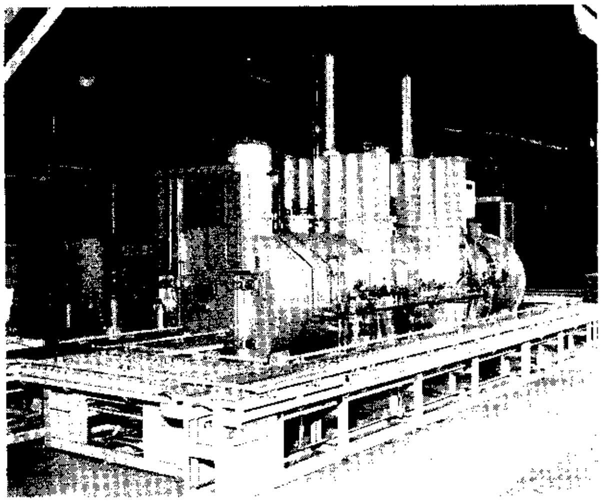

Photo 1 Appearance of vacuum annealing furnace

Table 1 Typical properties of chemial composition (%)

	Process	C	Si	Mn	P	S	Cr	Mo	V	$\underline{O}$	N
KIP 4100 V	Vac. ann.	0.02	0.03	0.64	0.02	0.02	1.07	0.27	—	0.15	0.001
KIP 4100 VS	Vac. ann.	0.02	0.03	0.62	0.02	0.02	1.13	0.27	—	0.10	0.001
KIP 4100	Gas red.	0.05	0.01	0.66	0.01	0.01	1.08	0.28	—	0.80	0.058
KIP 30 CRV	Vac. ann.	0.03	0.03	0.31	0.01	0.01	2.97	0.34	0.26	0.12	0.001
KIP 30 CRA	Gas red.	0.13	0.04	0.25	0.01	0.01	2.99	0.32	0.26	0.83	0.061

Table 2 Typical properties of particle size distribution (%)

Powder	Process \ Mesh	+60	−60/ +80	−80/ +100	−100/ +150	−150/ +200	−200/ +250	−250/ +325	−325
KIP 4100 V	Vac. ann.	tr	2.0	9.4	18.4	25.4	10.0	15.4	19.4
KIP 4100 VS	Vac. ann.	tr	0.9	12.8	28.9	28.7	9.2	12.5	7.0
KIP 4100	Gas ann.	tr	tr	5.7	21.4	23.7	13.2	14.4	21.6
KIP 30 CRV	Vac. ann.	tr	3.6	11.2	22.3	24.4	8.5	11.4	18.6
KIP 30 CRA	Gas apn.	tr	tr	0.2	12.7	26.1	9.7	17.3	34.0

Table 3 Typical properties of apparent density and flow rate

	Process	Apparent density (g/cm³)	Flow rate (sec/50 g)
KIP 4100 V	Vac. ann.	2.83	25.7
KIP 4100 VS	Vac. ann.	2.70	28.9
KIP 4100	Gas ann.	3.26	20.1
KIP 30 CRV	Vac. ann.	2.58	29.6
KIP 30 CRA	Gas ann.	2.97	25.0

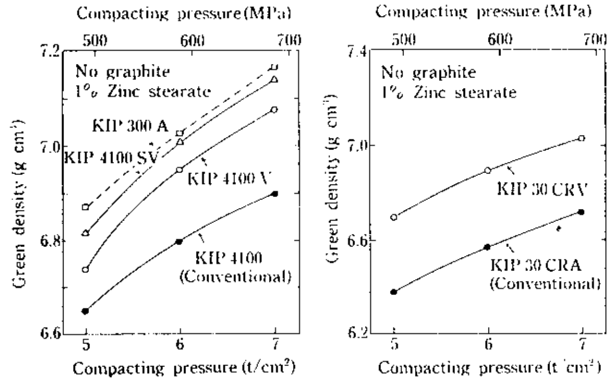

Fig. 3 Relation between compacting pressure and green density

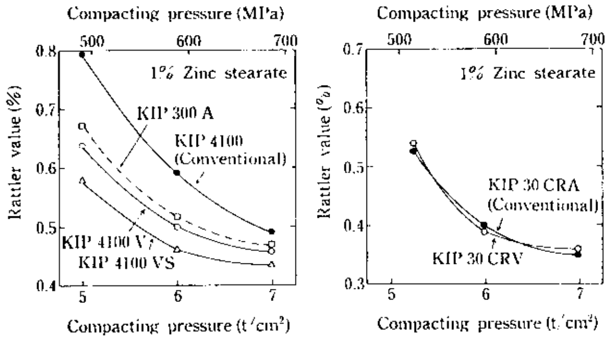

Fig. 4 Relation between compacting pressure and Rattler value

obtained through the conventional method. Table 1 also shows that C and N for KIP 4100 VS, KIP 4100 V, and KIP 30 CRV produced by vacuum annealing are much lower than those manufactured by the gas annealing method. These facts demonstrate that the vacuum annealing method is very effective for the deoxidizing, decarburizing, and denitrifying of alloyed steel powders containing elements which are difficult to reduce.

As shown in Figs. 3 and 4, KIP 4100 V, KIP 4100 VS, and KIP 30 CRV are superior with respect to compressibility and compactibility, and close in these respects to pure iron powder. The densities of powders compacted at 7 t/cm² with 1% Zn stearate added as a lubricant are as shown below.

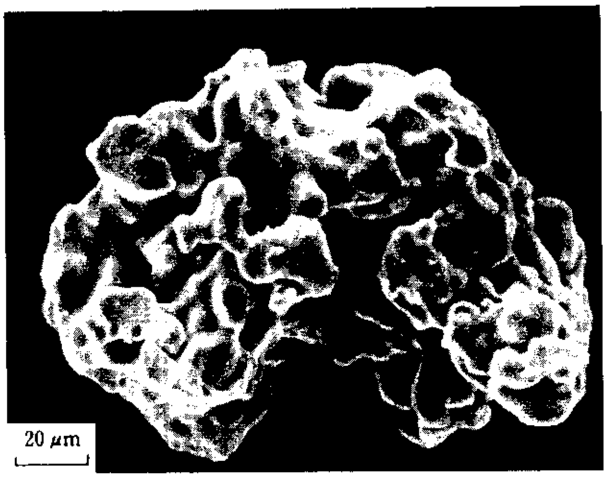

Photo 2 SEM of KIP 4100 V powder particles

KIP 4100 V :	7.08 g/cm³
KIP 4100 VS:	7.14 g/cm³
KIP 30 CRV:	7.02 g/cm³

The density of KSC's atomized pure iron powder KIP 300 A is 7.16 g/cm³ when compacted at the same pressure. The Rattler values of these products compacted at 7 t/cm² (with 1% Zn stearate added) are as follows:

KIP 4100 V :	0.46%
KIP 4100 VS:	0.44%
KIP 30 CRV:	0.36%
KIP 300 A :	0.47%

Alloyed steel powder produced by the vacuum annealing process is characterized by low O, low C, and low N and by excellent compactibility. The latter may be attributed to irregular particle contour, such as is shown in **Photo 2**.

Photo 3 shows the distribution of alloy components in the cross section of steel particles of KIP 4100 VS and KIP 4100, manufactured through the vacuum and gas annealing processes respectively. While the distribution of various components in KIP 4100 VS is uniform and no segregation is seen, KIP 4100 shows segregation of Mn, Cr, and O. This shows that the vacuum annealing process reduces the amount of Mn and Cr oxides, providing steel powder of homogeneous microstructure.

4.2 Effects of O, C, and N on Powder Properties

Figures 5, **6**, and **7** show the relationship of compacted powder density to contents of O, C and N in KIP 4100 V. Compacted powder density has been improved by the reduction of O, C, and N from the surface and interior of the steel powder.

5 Properties of Sintered and Quench-Annealed Materials

Properties of sintered and quench-annealed specimens of KIP 4100 VS and KIP 4100 were examined.[5)]

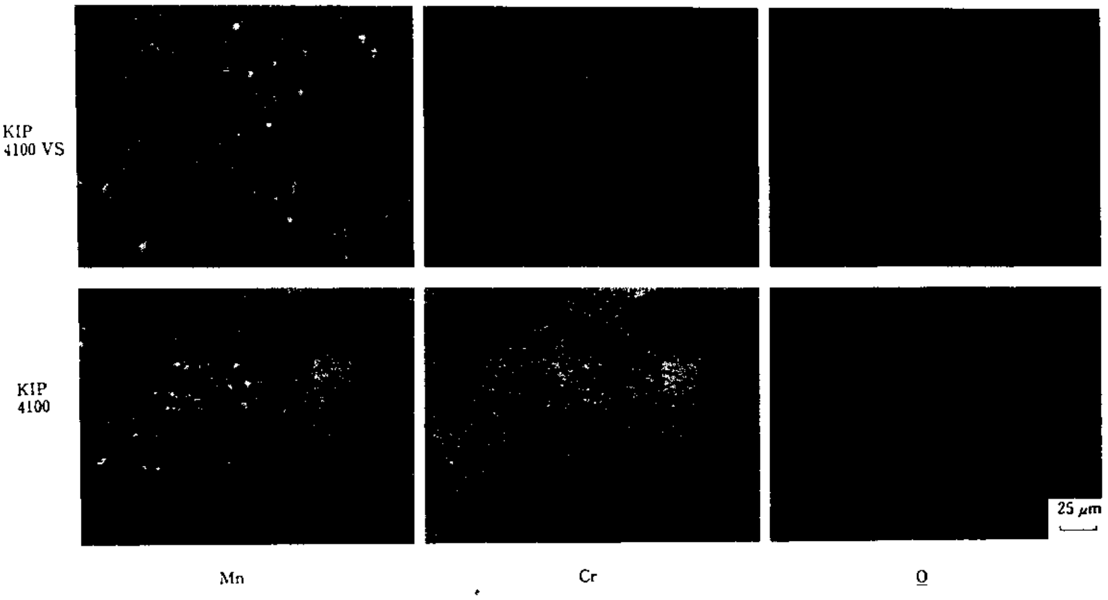

Photo 3 Comparison of Mn, Cr and O distribution between KIP 4100 VS and KIP 4100 sintered compacts

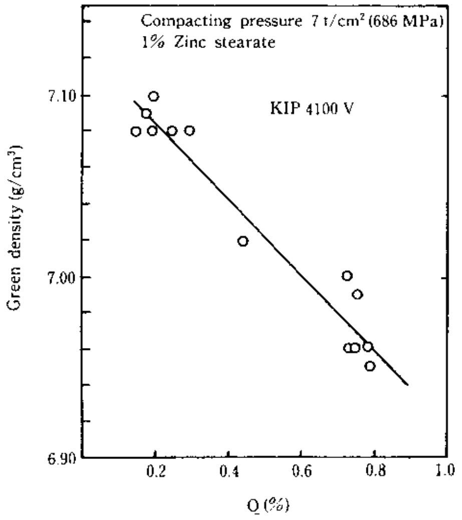

Fig. 5 Effect of O contents on green density

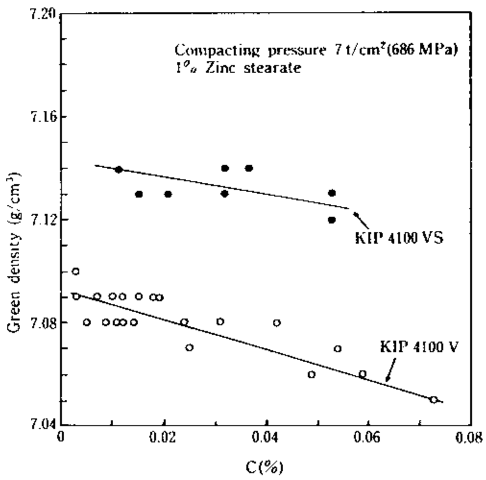

Fig. 6 Effect of C contents on green density

mens of KIP 4100 VS and KIP 4100 were examined.[5] The manufacturing process for the test specimens is shown in **Fig. 8**, and the results are described below.

(1) Contents of C and O

The relation between the addition of graphite and C and O contents is shown in **Fig. 9**. KIP 4100 VS, with its low O content, gives a high yield of C in the sintered sample. Further, O is constant regardless of the amount of graphite addition, and is lower than in conventional KIP 4100.

(2) Tensile Strength

The results of tension tests are shown in **Fig. 10**. The tensile strength of sintered KIP 4100 VS is 80 kgf/mm² (with 0.9% graphite added), which is about

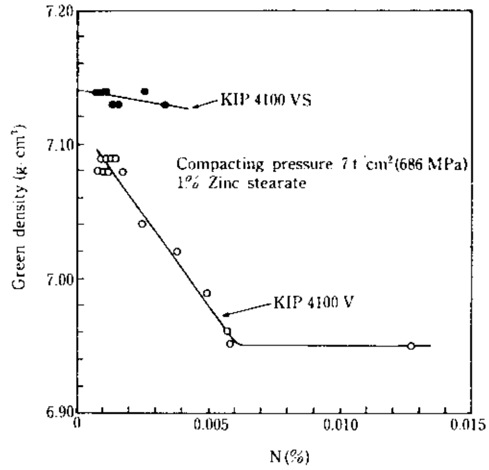

Fig. 7 Effect of N contents on green density

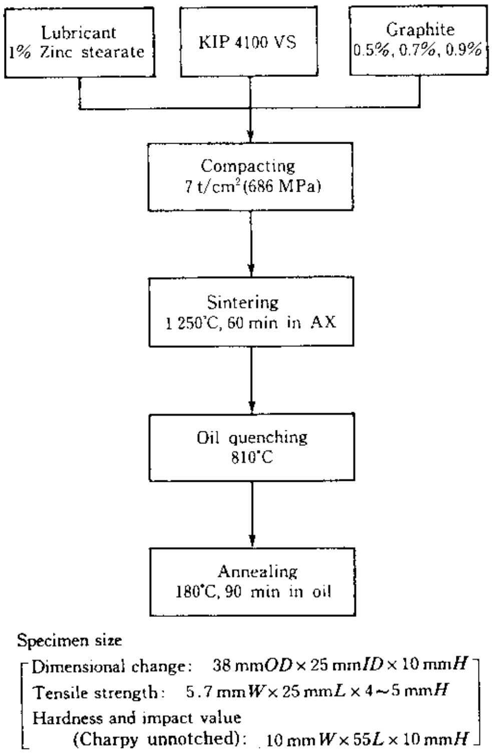

Fig. 8 Manufacturing process of test samples

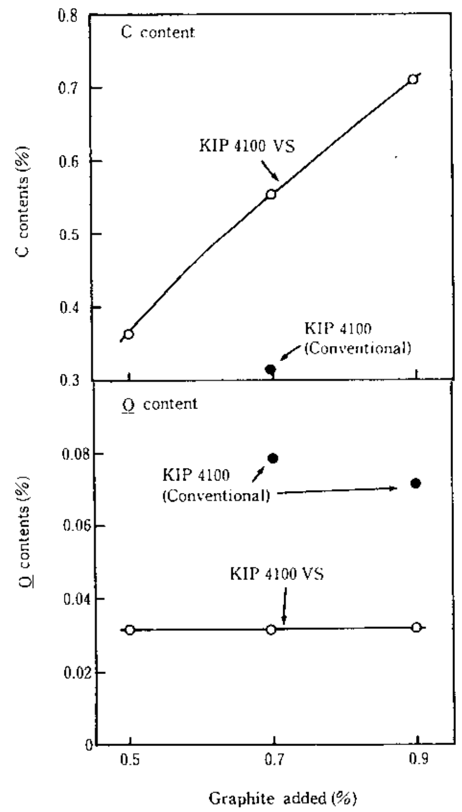

Fig. 9 Effect of graphite added on C and O contents in sintered compacts

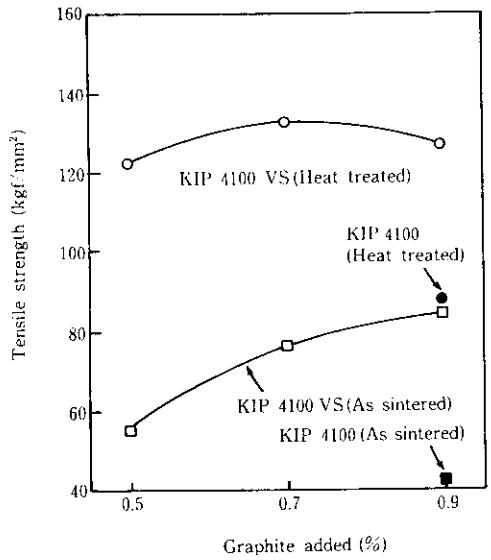

Fig. 10 Effect of graphite added on tensile strength

twice that of KIP 4100 produced by gas annealing. The tensile strength of KIP 4100 VS after heat treatment exceeds 130 kgf/mm² (with 0.7% graphite added), and is 1.5 times that of conventional sample.

(3) Toughness and Inclusions

The results of the impact test are shown in **Fig. 11**. KIP 4100 VS with reduced oxygen content and inclusions possesses high toughness, with that of sintered KIP 4100 VS about three times that of KIP 4100. Moreover, KIP 4100 VS provides high toughness even after heat treatment. Microscopic tests of sintered KIP 4100 VS and KIP 4100 reveal that the volume ratio of non-metallic inclusions in KIP 4100 VS is $2.8 \times 10^{-3}\%$, which is much lower than that of KIP 4100 ($8.4 \times 10^{-3}\%$), indicating a reduction of inclusions due to reduced oxygen content.

(4) Hardness

Figure 12 shows the results of the hardness test. The hardness of heat treated KIP 4100 VS is HRA 68, which is much better than that of KIP 4100.

(5) Dimensional Change

Figure 13 shows the effect of added graphite on dimensional change taking compacted powder as a standard. The dimensional change of KIP 4100 VS is −0.51% when sintered, and −1.11% when heat treated. The springback of KIP 4100 VS varies with the amount of graphite added: 0.5% with 0.237% graphite; 0.7% with 0.224%; 0.9% with 0.210%.

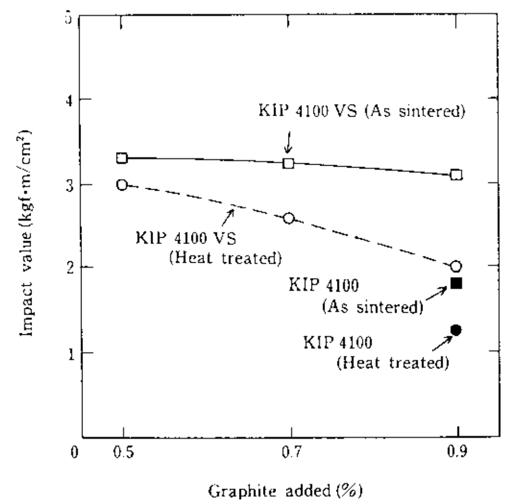

Fig. 11 Effect of graphite added on impact value

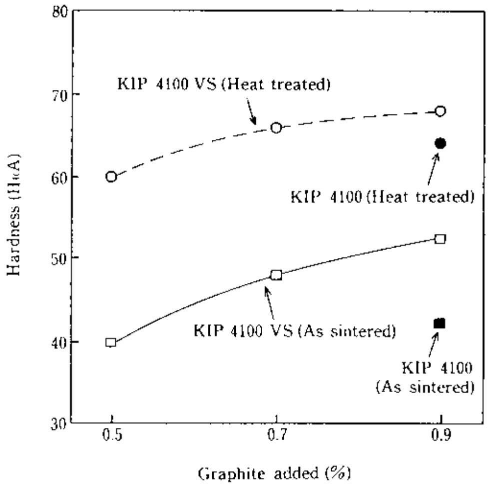

Fig. 12 Effect of graphite added on hardness

6 Conclusions

A water-atomization, vacuum annealing production line (capacity 100 t/month) has recently been constructed at the Chiba Works, and the production of steel powders KIP 4100 V and KIP 4100 VS, corresponding to AISI 4100, started. In low-alloyed steel powder containing Mn and Cr, the content of O is reduced through a vacuum annealing process in which carbon pre-alloyed in molten steel is used as the reducing agent. With KIP 4100 VS, the following results were obtained:

(1) The contents of O, C, and N in steel powder were very low: O, 0.10%; C, 0.02%; and N, 0.001%.

(2) The physical properties of compacted powder were very good: green density, 7.14 g/cm^3 and Rattler value, 0.44%, at a compacting pressure of 7 t/cm^2 (with 1% Zn-stearate added).

(3) Physical properties of sintered parts were excellent; the tensile strength of sintered and heat-treated material was 130 kgf/mm^2.

Since steel powder produced by the vacuum annealing process is excellent with respect to compressibility, compactibility, sintering, and annealing properties, as has been described above, application to automobile parts can be expected.

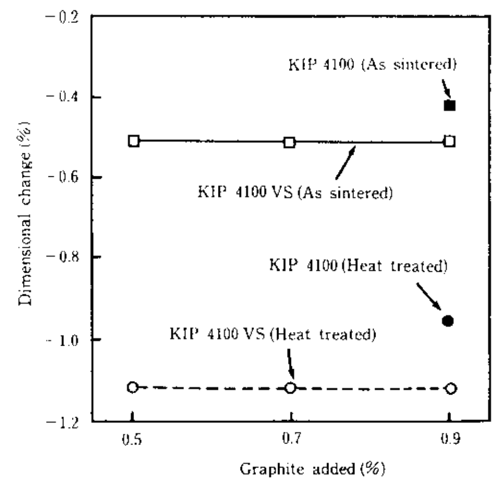

Fig. 13 Effect of graphite added on dimensional change

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