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(54) NITROGEN-CONTAINING POWDER METALLURGICAL TOOL STEEL

(71) We, KOBE STEEL LTD., a body corporate organised under the laws of Japan of 3—18, 1—chome, Wakinohama-cho, Fukiai-ku, Kobe-city, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a tool steel, particularly to a nitrogen-containing powder metallurgical steel (hereinafter referred to as "PM" steel), wherein the amounts of C, N and V are adjusted to the particular requirements of the steel.

It is known that the properties of tool steels containing alloying elements such as Cr, W and V can be improved by the incorporation of nitrogen into the steels [see, for example, Kobe Steel Technical Bulletin, R & D, Vol. 24 No. 3, pages 11 to 15, and Japanese Patent Applications (Laid-Open Specifications (Nos. 78606/74, 49109/75 and 49156/75]. These steels are widely used as jig materials such as die materials and as cutting tool materials because they have good wear resistance and good heat resistance. By a nitriding treatment, a nitride of the MX or M_6X (in which M represents an alloying element and X represents nitrogen) is formed, and this nitride is more stable than a carbide of the type MC or M_6C. Accordingly, the appropriate quenching temperature range is broadened and control of the heat treatment can be facilitated.

Further, the temper hardening characteristics are improved and a fine austenitic crystal structure can be obtained to improve the mechanical properties. Furthermore, the machinability of the steels can be improved.

According to Japanese Patent Publication No. 19774/1971, the addition of 0.05—0.35% N to a die steel for high temperature service contributes to an increase in the resistance to softening at high temperature, to suppress growth of the grain boundaries, and further contributes to suppress an undue formation of delta ferrite.

Most conventional nitrogen-containing tool steels have heretofore been prepared by a smelting process. When a smelting process is adopted for the production of nitrogen-containing tool steels, it is necessary to perform complicated steps such as the step of melting steel in a high-pressure nitrogen atmosphere or the step of throwing nitride into the molten steel. Further, according to the smelting process, since the amount of nitrogen included in the steel is small and it is difficult to form a fine carbonitride and to distribute it uniformily in steel, it is impossible to improve the properties to desirable levels.

As a means of overcoming the defects or limitations involved in the smelting process, methods have recently been proposed for obtaining nitrogen-containing tool steels by a powder metallurgical process or a powder forging process. In those methods, by utilizing the fact that powder has a large specific surface area (surface area/volume), and the fact that a powder-sintered body has a porous structure, an optional amount of nitrogen can be included in the steel by a simple means, for example, by adding nitrogen in advance to the starting powder or by adjusting the heating temperature the heating time or the nitrogen partial pressure in the treatment atmosphere at the sintering step. It is expected that nitrogen will be finely and uniformly distributed in steels according to these methods.

In conventional nitrogen-containing PM steels, the machinability is not as highly improved as might be expected, as is apparent from Japanese Patent Publication No. 37810/1972. N is not a desirable element for stabilizing retained austenite when the steel is to be used for gauges (see, for example, Japanese Patent Publication No. 9900/1972).

Instead, the machinability is degraded by the incorporation of nitrogen into the steels. Accordingly, it is often said that the value of nitrogen-containing, high-speed steels produced by a powder metallurigal process is questionable. However, several nitrogen-containing, high-speed PM steels which have recently been put into practical use, have exhibited good machinability and good wear resistance in combination. The reason for this has not been elucidated. In particular, the relation between amounts of alloying elements which impart excellent machinability to steel and the amount of nitrogen enrichment is not clarified. Therefore, the kinds of steels which are enriched with nitrogen for the production of high-speed PM steels and which are usable are drastically limited. For example, Kobe Steel Technical Bulletin, R & D. Vol. 24, No. 3, page 10 discloses that, when 0.4—0.5% N is added to Mo-type high-speed PM steels (JIS SKH 9 and modified JIS SKH 55), the machinability is remarkably improved.

Taking advantage of the fact that N addition is very advantageous for fine and uniform carbide, we have sought to improve the various properties required in tool steels, particularly the wear resistance and impact property with respect to various steel compositions. This has led to the tool steel of the present invention.

An object of the present invention is to solve the problems encountered with conventional nitrogen-containing PM tool steels. Thus, it is an object of the present invention to provide nitrogen-containing PM tool steels having excellent wear resistance and excellent impact properties. These and the other features of the present invention can be attained according to the present invention.

The present invention provides a nitrogen-containing powdern metallurgical tool steel which comprises; at least 0.40% N, 1.6—15% V, C in an amount satisfying the relationship of:

$$0.2 + 0.2\ V(\%) \leqq (C + N) < 0.5 + 0.2\ V(\%),$$

and a proportion of at least one element consisting of up to 15% Cr, up to 10% Mo, up to 20% W or up to 15% Co.

Reference is now made to the accompanying drawings in which:

Fig. 1 is a graph showing the relationship between the nitrogen content and the properties of JIS SKH 9 steels containing approximately 0.5% C;

Fig. 2 is a graph showing the relationship between the (C+N) content and the properties of JIS SKH 9 steels containing 0.1—0.7% C;

Fig. 3 is a graph showing the relationship between the (C+N) content and the properties of steels containing 0.3—0.9% C;

Fig. 4 is a graph showing the relationship between the (C+N) content and the properties of steels containing 1.7—2.5% C;

Fig. 5 is a graph showing the relationship between the (C+N) content and the properties of steels containing 0.2—0.9% C;

Fig. 6*a* is a photograph showing the microstructure of steel prepared by a powder metallurgical process; and

Fig. 6*b* is a photograph showing the microstructure of steel prepared by a smelting process.

High-speed steels are characterized by their excellent wear-resistance and heat-resistance because they contain large amounts of Mo, W and V which are carbide-forming elements rather than Fe. Further, they have a relatively good impact property, so that they have conventionally been used mainly in cutting tools.

From the viewpoint of the total characteristics of steels including wear-resistance, heat-resistance, pressure-resistance and impact property, high-speed steels are superior to tool materials such as those of low and high temperature dies, and are used in working tools for low- and high-temperature service in addition to cutting tools.

In this case, it is important to improve impact properties without degrading wear resistance. To this end, heat treatment such as low temperature hardening is often adopted. On the other hand, lowering the C content is advantageous for improving the impact property from the compositional viewpoint but adversely affects wear resistance.

We therefore conducted the following experiments seeking the development of tool steels having both a good wear resistance and a good impact property.

A typical example of a steel powder corresponding to JIS SKH 9 (comprising 0.5% C, 4.3% Cr, 5.1% Mo, 6.0% W and 2.0% V) is used. Nitrogen is incorporated in this steel and high-speed steels differing in nitrogen content are prepared. In these high-speed steels, the influence of the nitrogen content on the wear resistance and the impact property was examined and the results shown in Fig. 1 were obtained.

As is apparent from the results shown in Fig. 1, the wear resistance is remarkably improved when the nitrogen content is at least 0.40% and while the impact value is good when the N content is less than 0.40%, it is apparently degraded when the N content is over 0.40%.

Carbon which is an essential element of high-speed steels has general properties which are quite similar to those of nitrogen which is an additional element. Each of these elements has a very small atomic number of 6 or 7 and is an atom of the interstitial type having a tendency readily to form an alloy compound.

Accordingly, it is deemed reasonable to adjust or to regulate the nitrogen content in combination with the carbon content, for example, relying on such factors as the (C+N) content, or the C/N ratio irrespective of the C content. Moreover, it is desired to regulate or to adjust the nitrogen content after due consideration of the contents of elements which have been admitted in the art as elements capable of forming carbides together with C and N in high-speed steels, particularly V.

In view of the foregoing, as illustrated in the Examples hereinafter, steel powders corresponding to JIS SKH 9 or 10, which differ in carbon content, were prepared and nitrogen was incorporated in these steel powders in an amount of at least 0.40% necessary for improving the wear resistance of the steels. Then, high-speed steels were prepared form these powders by the powder metallurgical process, and they were tested with respect to the wear resistance and the impact property, and the results obtained are shown in Figs. 2—5 of the drawings.

Fig. 2 illustrates the results obtained with respect to the steels corresponding to JIS SKH 9 containing 1.95—2.04% V. It is seen from Fig. 2 that, if the (C+N) content is more than 0.6%, the wear resistance is remarkably improved. At the same time, the impact property is good if the (C+N) content is less than 0.9%. Thus, in a nitrogen-containing, high-speed PM steel which corresponds to JIS SKH 9, the (C+N) range appropriate for improving the wear resistance without degrading the impact property is 0.6—0.9%.

Fig. 3 illustrates the results obtained with steels corresponding to JIS SKH 10 containing 4.45—4.53% V. From Fig. 3, it is apparent that a suitable range of (C+N) content is 1.1—1.4%.

Fig. 4 illustrates the results obtained with steels having an increased V content, namely 4% Cr—3.5% Mo—10% W—12% V steels. In this case, a suitable range of (C+N) content is 2.6—2.9%.

Further, Fig. 5 illustrates the results obtained with the steels corresponding to AISI A7 containing 4.78—4.83% V and for use in cold working tools. In this case, a suitable range of (C+N) content is 1.15—1.45%.

If the foregoing experimental results obtained with respect to various high-speed PM steels are collectively considered mainly in view of the (C+N) and V contents, it is apparent that, in order to improve the impact property without degrading the wear resistance, the following requirement must be satisfied:

$$0.2 + 0.2\ V(\%) \leqq (C + N) < 0.5 + 0.2\ V(\%).$$

According to this requirement, if the V content exceeds 15%, the toughness ordinarily decreases drastically because a vanadium-type carbonitride is coarsened, and, in such a case, the above relationship which defines a suitable range of (C+N) content suitable for machinability, heat-treatment properties, and mechanical properties is not satisfied.

Moreover, if the vanadium content is above 15%, since a vanadium-type carbonitride is coarsened, the grindability and the forging property are very substantially degraded. If the vanadium content is lower than 1.6%, it becomes practically difficult to enrich with nitrogen to an extent higher than 0.4%. Therefore, the vanadium content must be at least 1.6%. No significant improvement of the machinability is attained if the nitrogen content is lower than 0.40%. In the present invention, it is preferred that the nitrogen content should be at least 0.45%.

As is apparent from the foregoing experimental results, the above-mentioned relationship, namely an appropriate range of the (C+N) content, is not changed in various high-speed steels differing in the contents of such metals as Cr, Mo, W and Co.

In the PM tool steels according to the present invention, there are tool steels called alloy tool steels containing relatively small amounts of Cr, Mo, W, Si, Mn and Ni with the appropriate amounts of N, C and V, there are other types of tool steels called high-speed steels containing increased amounts of those alloying elements, and there are also tool steels containing intermediate amounts of those elements. In general, in tool steels, Cr is added in an amount of up to 15%, Mo is added in an amount of up to 10%, W is added in an amount of up to 20% and C is added in an amount of up to 15%. Further, according to need, up to 3% Ni, up to 1% Mn, and up to 1% Si may be added. Furthermore, up to 2% Zr, up to 5% Nb, up to 1% B may also be added.

The tool steels mentioned above are widely adopted as metal moulds such as press tools, trimming dies, drawing dies, and as jigs such as chisels, punches and gauges.

The present invention will now be further described with reference to the following Examples.

Example 1.

Gas atomized steel powders corresponding to JIS SKH 9 and differing in carbon content were packed in mild steel cans, subjected to degasification and nitriding treatments, and then compression-formed by a hot isostatic press involving a heat treatment. The preparation conditions and the tests for determining the wear resistance and impact property are illustrated below.

1) Preparation Conditions

(a) Chemical Composition and Grain Size of Starting Powder.

The starting powders used are shown in Table 1.

(b) Nitriding Treatment

The nitriding treatment was conducted at 1150°C for 2 hours in a nitrogen atmosphere. The pressure of the atmosphere was appropriately controlled to adjust the nitrogen content in the product steel.

(c) Hot Isostatic Press Treatment

Hardening: 1100°C × 2 hours under 2000 atm

TABLE 1

Kind of Steel	Composition (%)											Grain Size
	C	Si	Mn	P	S	Cr	Mo	W	V	O	N	
A (0.7% C)	0.70	0.29	0.27	0.01	0.03	4.30	5.01	6.12	1.95	0.010	0.021	smaller than 80 mesh
B (0.5% C)	0.49	0.25	0.24	0.01	0.04	4.35	5.12	6.06	2.00	0.030	0.015	smaller than 80 mesh
C (0.3% C)	0.32	0.31	0.32	0.01	0.03	4.11	4.97	6.15	2.04	0.035	0.018	smaller than 80 mesh
D (0.1% C)	0.11	0.32	0.29	0.01	0.02	4.05	4.91	6.08	2.01	0.040	0.017	smaller than 80 mesh

(d) Heat Treatment

Hardening: 1150°C × 5 minutes (Oil Quenching)

Tempering: repeated 2—4 times with heating pattern of 450—550°C × 1.5 hours, intending to obtain hardness of HRC 59—60.

2) Test Conditions

(a) Wear resistance test

Load: 4.5 Kg

Friction Length; 550 m

Friction Speed: 2.5 m/sec

Material to be applied: JIS SCM 4 (Q.T.), H_B300—350

Lubricant: no

(b) Impact Test

R-notch 10 mm square Charpy Test

3) Results of Test

Test results are shown in Fig. 2 of the accompanying drawings. As is apparent from the results shown in Fig. 2, in nitrogen-containing, high-speed PM steels containing 2% V, in order to improve the wear resistance without degrading the impact property, the nitrogen content must be at least 0.04%, and a suitable (C+N) content is 0.6—0.9%. If the nitrogen content is below 0.4%, the nitriding effect is not adequate. If the (C+N) content is below 0.6% there are only few nitride precipitates and the wear resistance of the steel is degraded, while if over 0.9% the decrease in impact value is drastic.

With respect to a nitrogen-containing, high-speed PM steel which is shown in Fig. 2 and comprises 0.3% C and 0.4% N, an intermittent cutting test with a cutting tool of this steel was conducted under the following conditions:

Tool hardness: HRC 64

Tool shape: 0°, 15°, 6°, 6°, 15°, 10 R

Cutting speed: 25 m/min

Cut depth: 1.5 mm

Feed rate: 0.2 mm/revolution

Material machined: JIS SCM 4 (Q.T.) H_B 250—270

The cutting property of this tool was confirmed to be equivalent to that of a cutting tool consisting of JIS SKH 9 high speed steel produced by smelting.

Example II.

Atomized steel powders corresponding to JIS SKH 10 and differing in carbon content as shown in Table 2 were used as the starting powders and formed into nitrogen-containing, high-speed PM steels in the same manner as described in Example I. The wear resistance and the impact value were measured and the results obtained are shown in Fig. 3.

As is apparent from the results shown in Fig. 3, a (C+N) content effective for improving the wear resistance without degrading the impact value is 1.1—1.4%. But, when the (C+N) content is within the range of 1.1—1.4% if the N content is approximately 0.3%, the the improvement in the wear resistance is inadequate as shown in Fig. 3 of the drawings.

TABLE 2

Kind of Steel	Composition (%)											Grain Size
	C	Si	Mn	P	S	Cr	W	V	Co	O	N	
E (0.9% C)	0.91	0.25	0.25	0.02	0.03	3.91	12.3	4.53	4.85	0.035	0.031	smaller than 28 mesh
F (0.6% C)	0.59	0.31	0.29	0.01	0.03	4.12	12.8	4.48	4.92	0.021	0.063	smaller than 28 mesh
G (0.3% C)	0.31	0.32	0.25	0.02	0.04	4.07	12.5	4.45	5.01	0.036	0.040	smaller than 28 mesh

Example III.

Gas-atomized steel powders containing approximaely 12% V and differing in carbon content as shown in Table 3 were used as the starting powders and formed into nitrogen-containing, high-speed PM steels in the same manner as described in Example I. The wear resistance and the impact value were measured and the results obtained are shown in Fig. 4.

TABLE 3

Kind of Steel	Composition (%)											Grain Size
	C	Si	Mn	P	S	Cr	Mo	W	V	O	N	
H (2.5% C)	2.50	0.29	0.31	0.01	0.02	4.01	3.56	10.3	12.2	0.041	0.18	smaller than 80 mesh
I (2.0% C)	2.01	0.29	0.30	0.01	0.02	4.04	3.61	9.8	12.3	0.030	0.18	smaller than 80 mesh
J (1.7% C)	1.69	0.35	0.30	0.02	0.03	4.09	3.75	10.4	11.8	0.050	0.15	smaller than 80 mesh

As is apparent from the results shown in Fig. 4, a suitable (C+N) content effective for improving the wear resistance without degrading the impact value is 2.6—2.9%.

Example IV.

Gas-atomized steel powders corresponding to AISI A7 shown in Table 4 were used as the starting powders and formed into nitrogen-containing, high-speed PM steels in the same manner as described in Example I. The wear resistance and the impact value were measured and the results obtained are shown in Fig. 5.

TABLE 4

Kind of Steel	Composition (%)											Grain Size
	C	Si	Mn	P	S	Cr	Mo	W	V	O	N	
K (0.9% C)	0.92	0.31	0.32	0.02	0.03	5.20	0.96	1.06	4.78	0.040	0.046	smaller than 28 mesh
L (0.6% C)	0.61	0.25	0.29	0.02	0.03	5.12	1.05	0.96	4.81	0.041	0.038	smaller than 28 mesh
M (0.3% C)	0.29	0.35	0.35	0.02	0.04	5.30	1.03	1.05	4.83	0.035	0.035	smaller than 28 mesh

As is apparent from the results shown in Fig. 5, the (C+N) content effective for improving the wear resistance without degrading the impact value is 1.15—1.45%.

Example V.

Two kinds of steels corresponding to JIS SKH 9 and containing a relatively small amount of nitrogen, which are prepared by a powder metallurgical process and by a smelting (melting + forging) process, respectively, were tested with respect to the wear resistance and the impact property. The chemical compositions of these steels are shown in Table 5.

TABLE 5

Kind of Steel	Composition (%)										
	C	Si	Mn	P	S	Cr	Mo	W	V	O	N
N (PM Steel JIS SKH 9)	0.91	0.30	0.30	0.01	0.03	4.15	4.91	6.03	1.98	0.006	0.02
O (Smelted Steel JIS SKH 9)	0.87	0.31	0.28	0.02	0.03	4.06	4.89	6.12	1.96	0.004	0.03

The results of the tests are shown in Table 6.

TABLE 6

Kind of Steel	Relative amount of wear ($mm^3/m.Kg$)	Impact value ($Kg.m/m^2$)
N	2.2×10^{-3}	5.5
O	2.1×10^{-3}	4.2

As a result, the impact value of the PM steel (N) is improved, because the microstructure of the PM steel is uniform and fine compared with the microstructure of the smelted steel (O), as is apparent from Fig. 6*a* and Fig. 6*b*.

Example VI.

A gas-atomized steel powder corresponding to JIS SKH 10, containing 1.5% C and 0.4% N is tested according to Example I. The chemical composition is shown in Table 7, and the results obtained are shown in Table 8.

TABLE 7

Kind of Steel	Composition (%)											
	C	Si	Mn	P	S	Cr	Mo	W	V	Co	O	N
P (N containing PM steel JIS SKL 10)	1.51	0.15	0.29	0.02	0.03	3.98	–	11.8	4.51	4.71	0.005	0.40

TABLE 8

Kind of Steel	Relative amount of wear mm^3/mKg	Impact value ($Kg.m/cm^2$)
P	2.3×10^{-4}	0.53

As is apparent from Table 8, the amount of wear and the impact value are the same as those of the steels containing 1.7% (C+N) in Fig. 3.

It should be noted that Steels N, O and P are outside the limitations of the present invention and are shown for comparison with the steels of the present invention.

As is readily apparent from the foregoing illustration, in the nitrogen-containing PM tool steel according to the present invention, an excellent wear resistance and an excellent impact property are obtained by adjusting and controlling the content of C, N and V so that the following requirements are satisfied:

$N \geqq 0.40\%$, more preferably $N \geqq 0.45\%$, $1.6 \leqq V \leqq 15\%$

and $0.2 + 0.2\ V(\%) \leqq (C + N) < 0.5 + 0.2\ V(\%)$.

Further, the steel of the present invention may contain a proportion of at least one element consisting of up to 15% Cr, up to 10% Mo, up to 20% W and up to 15% Co.

In addition, according to need, up to 3% Ni, up to 1% Mn and up to 1% Si may be incorporated in the steel. Furthermore, the steel may contain up to 2% Zr, up to 5% Nb and up to 1% B.

WHAT WE CLAIM IS:—

1. A nitrogen-containing high-speed, tool steel produced by the powder metallurgical process, which steel comprises: at least 0.40% N, 1.6—15% V, C in an amount satisfying the relationship of:

$$0.2 + 0.2\ V(\%) \leqq (C + N) < 0.5 + 0.2\ V(\%)$$

and a proportion of at least one element consisting of up to 15% Cr, up to 10% Mo. up to 20% W, or up to 15% Co, with the balance iron together with any inevitable impurities.

2. A nitrogen-containing, high-speed tool steel as set forth in claim 1, wherein at least 0.45% N is present.

3. A modification of a nitrogen-containing, high-speed tool steel as set forth in Claim 1, wherein said steel further comprises a proportion of at least one element consisting of up to 3% Ni, up to 1% Mn, or up to 1% Si.

4. A modification of a nitrogen-containing, high-speed tool steel as set forth in Claim 1, wherein said steel further comprises a proportion of at least one element consisting of up to 2% Zr, up to 5% Nb or up to 1% B.

5. A nitrogen-containing, high-speed tool steel as claimed in Claim 1, substantially as herein described with reference to the accompanying drawings and/or any of the specific examples.

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1583878 COMPLETE SPECIFICATION

4 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

Fig. 1.

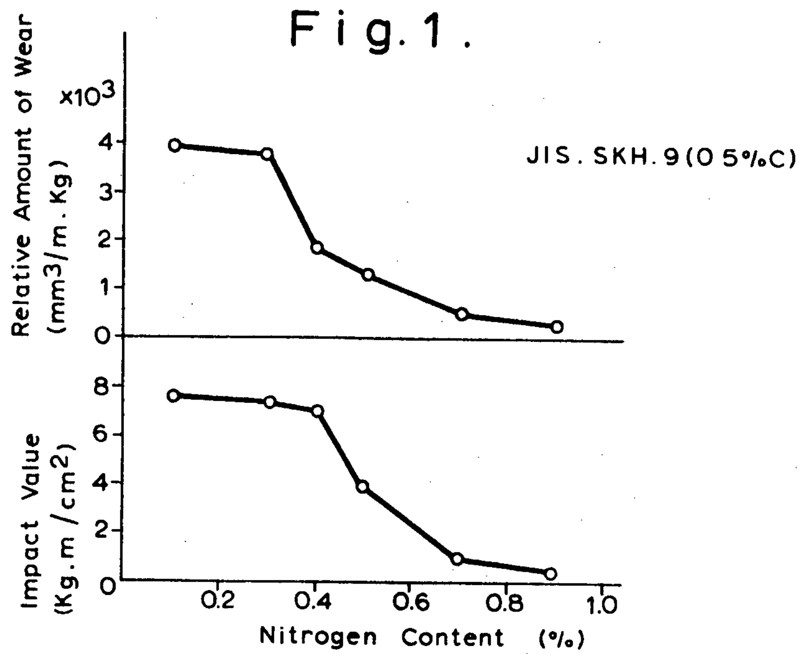


Fig. 2.

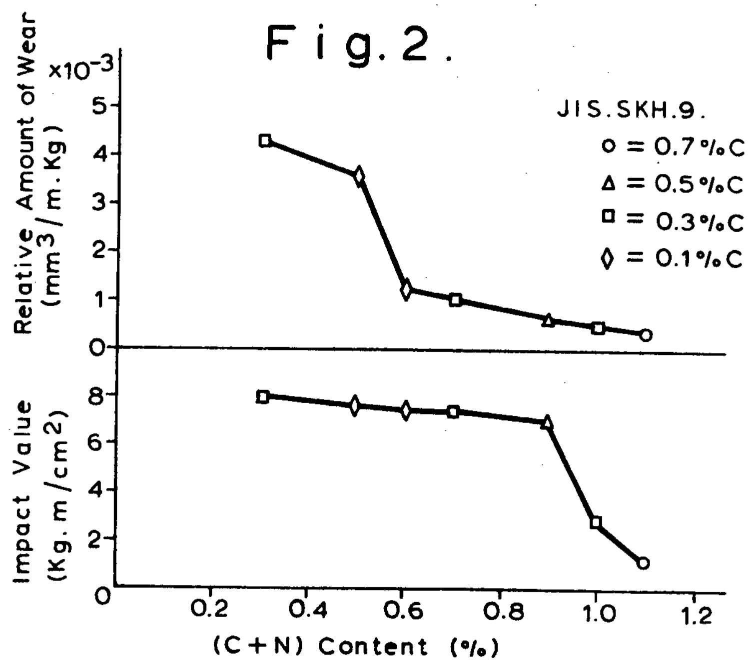


Fig. 3.

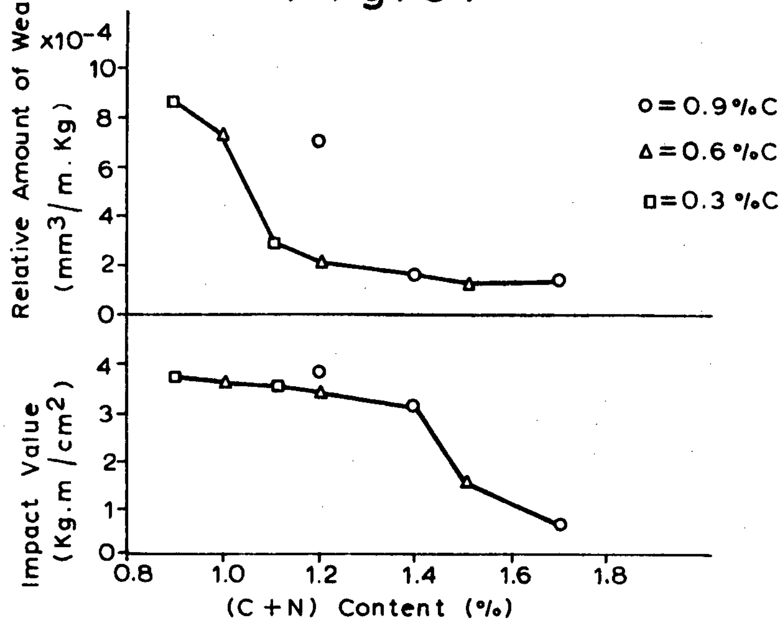

Relative Amount of Wear (mm3/m. Kg)
x10-4
10
8
6
4
2
0
Impact Value (Kg.m/cm2)
4
3
2
1
0
0.8
1.0
1.2
1.4
1.6
1.8
(C+N) Content (%)
o = 0.9 %C
Δ = 0.6 %C
□ = 0.3 %C

Fig. 4.

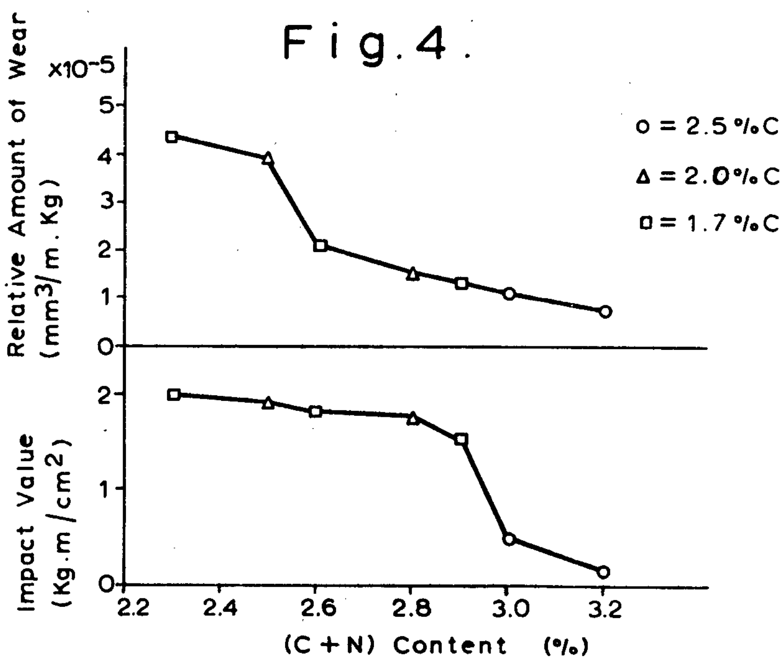
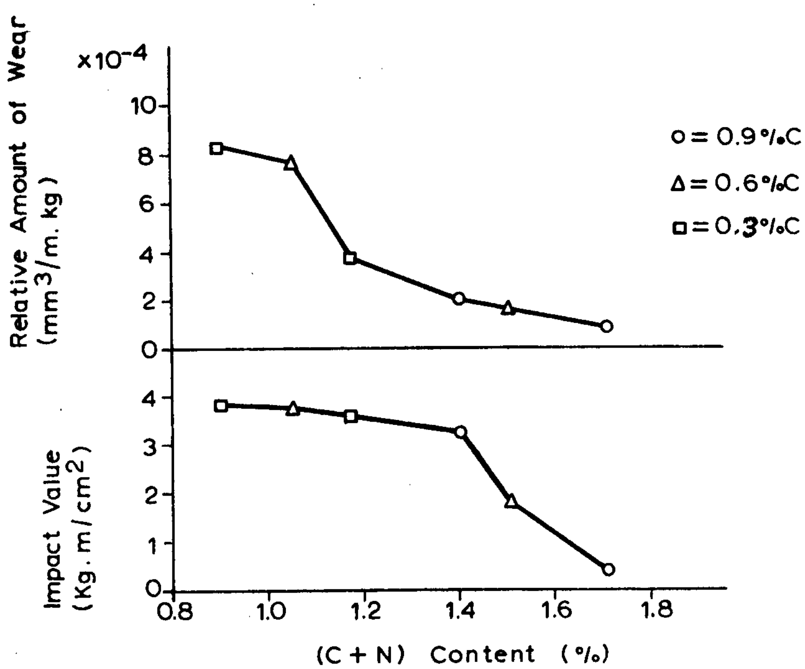
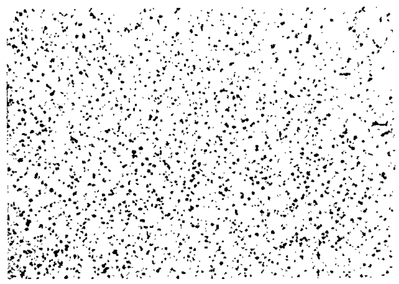

Relative Amount of Wear (mm3/m. Kg)
x10-5
5
4
3
2
1
0
Impact Value (Kg.m/cm2)
2
1
0
2.2
2.4
2.6
2.8
3.0
3.2
(C+N) Content (%)
o = 2.5 %C
Δ = 2.0 %C
□ = 1.7 %C

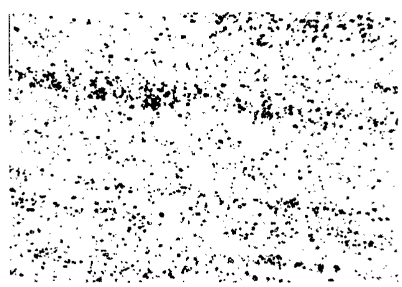
Fig. 5.


Relative Amount of Wear (mm3/m. kg)
x10-4
10
8
6
4
2
0
4
3
2
1
0
Impact Value (Kg. m/cm2)
0.8
1.0
1.2
1.4
1.6
1.8
(C + N) Content (%)
o = 0.9%C
Δ = 0.6%C
□ = 0.3%C



(x400)

Fig. 6a



(x400)

Fig. 6b