

July 17, 1973

AKIO HARA ET AL

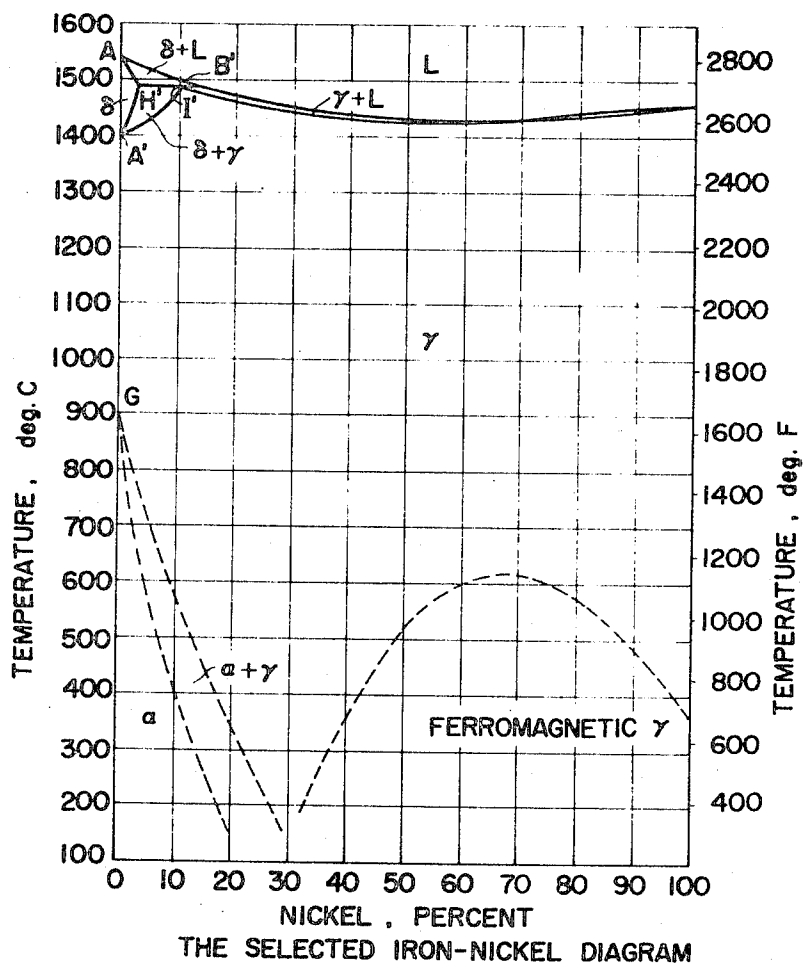
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HIGH STRENGTH METAL BONDED TUNGSTEN CARBIDE BASE COMPOSITES

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11 Sheets-Sheet 1

FIG. 1



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HIGH STRENGTH METAL BONDED TUNGSTEN CARBIDE BASE COMPOSITES

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FIG. 2

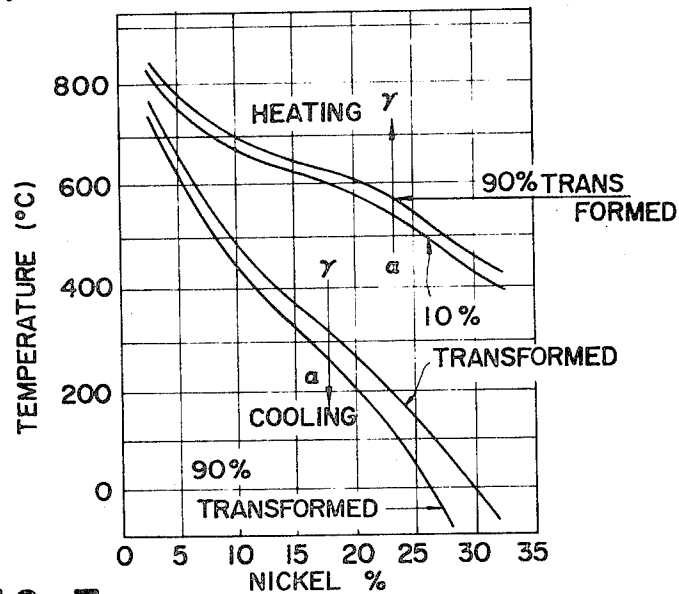
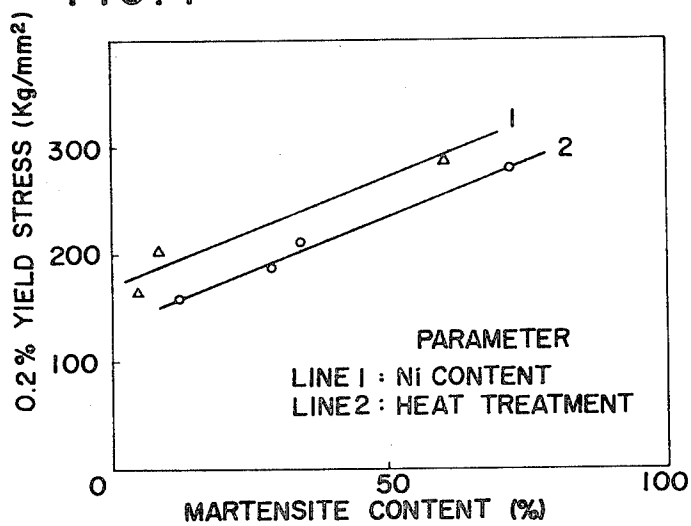


FIG. 7



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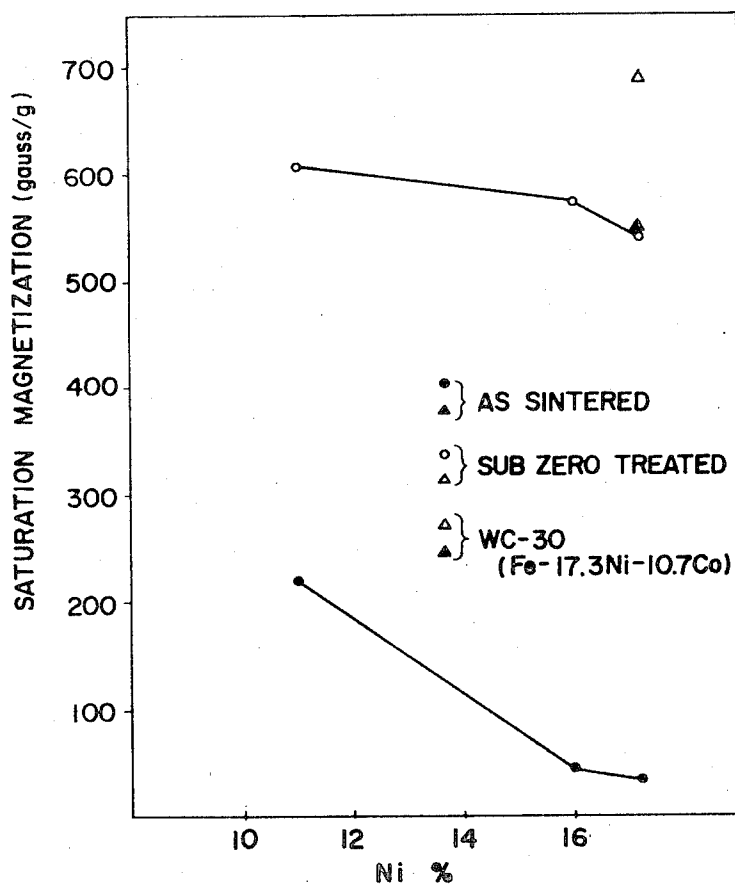
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HIGH STRENGTH METAL BONDED TUNGSTEN CARBIDE BASE COMPOSITES

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FIG. 3



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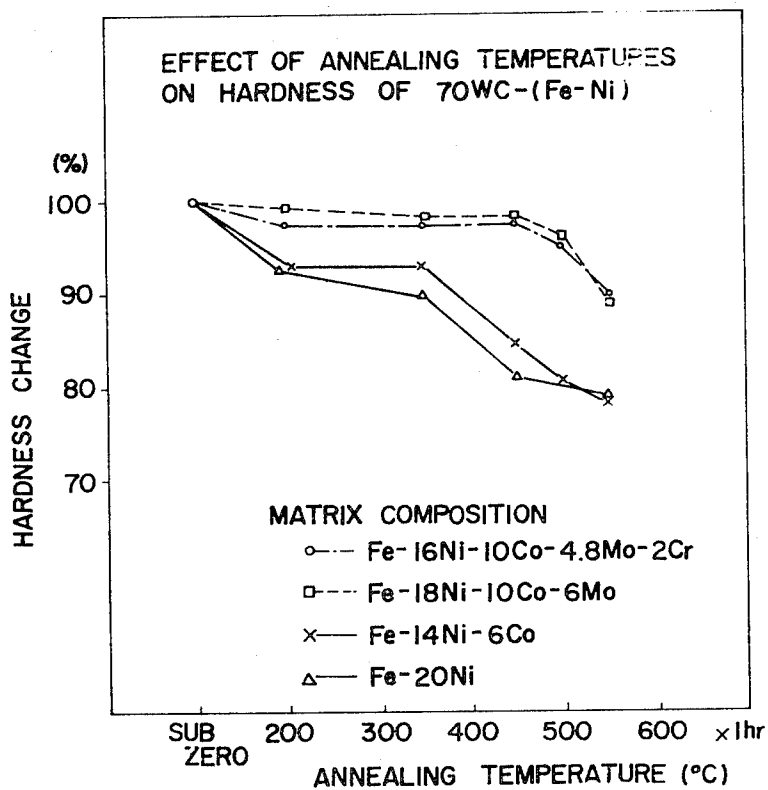
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FIG. 4



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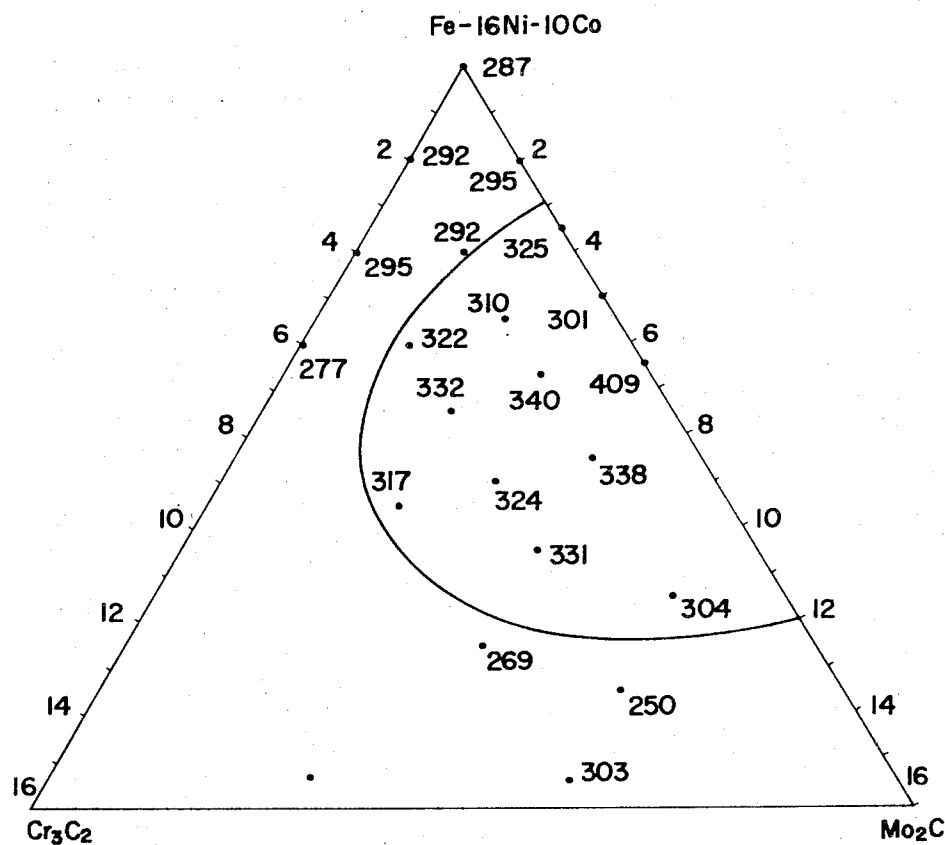
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HIGH STRENGTH METAL BONDED TUNGSTEN CARBIDE BASE COMPOSITES

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FIG. 5



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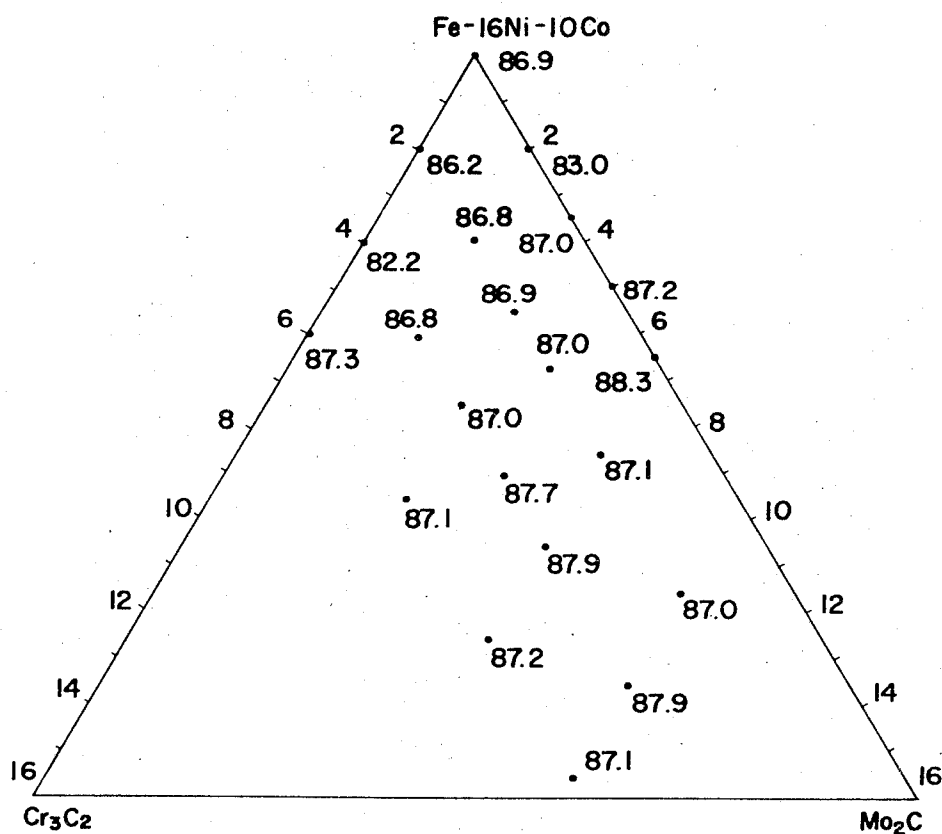
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FIG. 6



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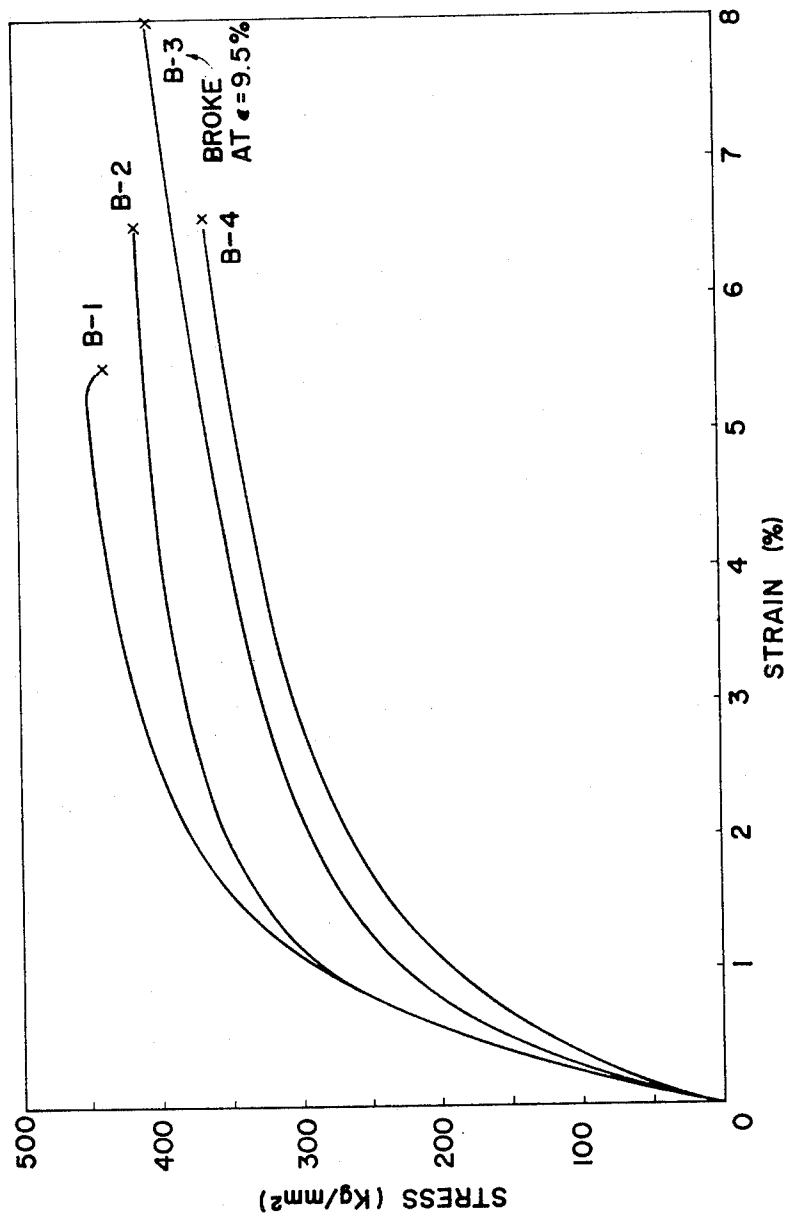
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HIGH STRENGTH METAL BONDED TUNGSTEN CARBIDE BASE COMPOSITES

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FIG. 8



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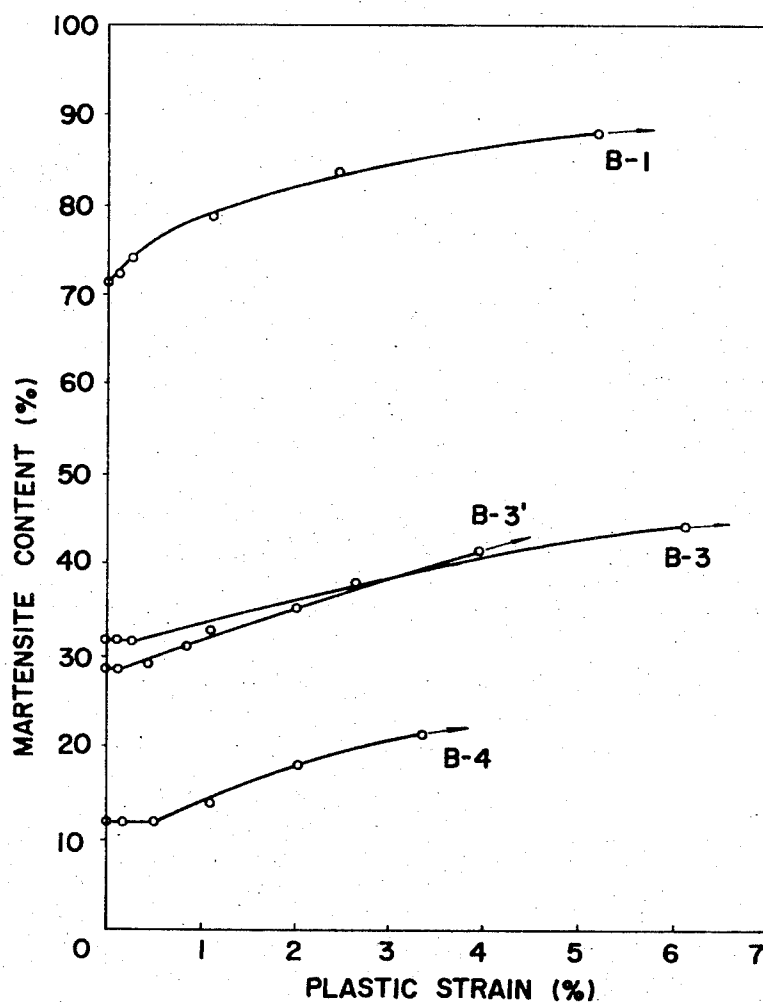
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HIGH STRENGTH METAL BONDED TUNGSTEN CARBIDE BASE COMPOSITES

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FIG. 9



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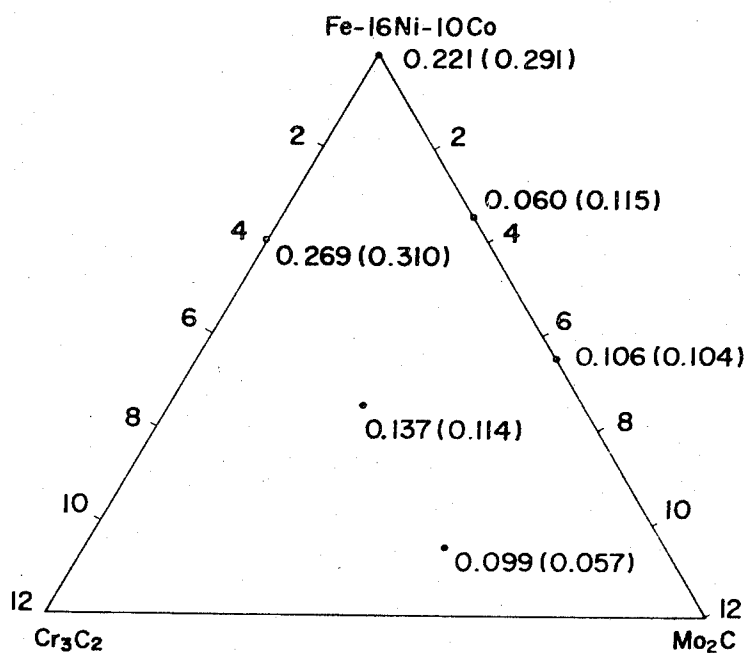


FIG. 10

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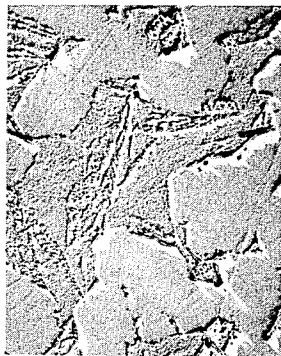
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HIGH STRENGTH METAL BONDED TUNGSTEN CARBIDE BASE COMPOSITES

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FIG. II



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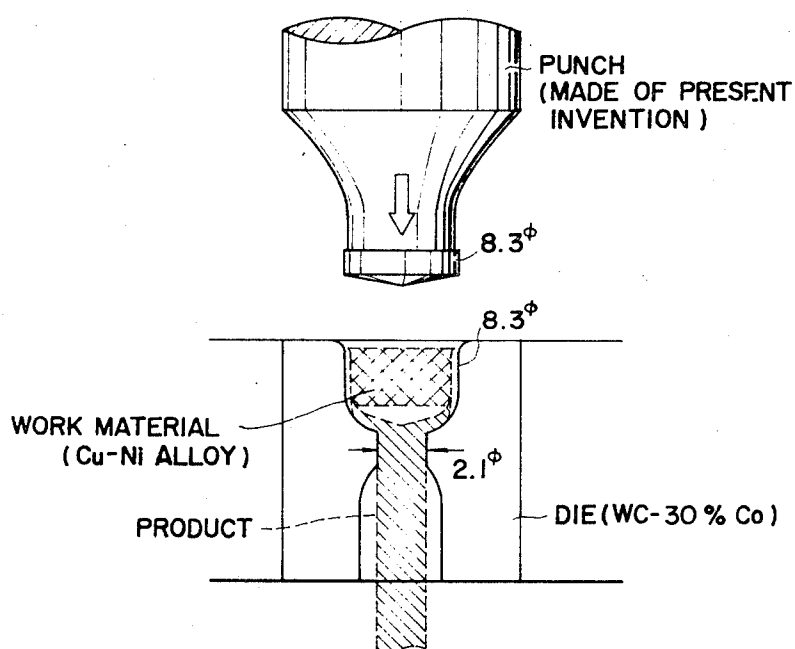
HIGH STRENGTH METAL BONDED TUNGSTEN CARBIDE BASE COMPOSITES

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FIG. 12

TEST RESULT OF PUNCHES



LIFE OF THE PUNCH

HSS (SKH9)	500 PC'S
PRESENT INVENTION	45000 ~ 50000 PC'S

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HIGH STRENGTH METAL BONDED TUNGSTEN CARBIDE BASE COMPOSITES

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Claims priority, application Japan, Feb. 18, 1970, 45/13,399; July 31, 1970, 45/67,646

Int. Cl. B22f 3/00

U.S. Cl. 29—182.7

6 Claims

ABSTRACT OF THE DISCLOSURE

A high strength and tough sintered tungsten carbide base composite consisting essentially of metal carbides, containing tungsten carbide as a principal component, and from 10 to 50 weight percent of a steel binder consisting essentially of 4 to 30 weight percent nickel and/or 1 to 25 weight percent cobalt, 1 to 15 weight percent molybdenum and/or 1 to 10 weight percent chromium.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to tungsten carbide base composites having improved strength and toughness and more particularly to tungsten carbide base composites bonded with steel binders consisting essentially of iron-nickel or iron-cobalt alloys having added thereto molybdenum and/or chromium.

Description of the prior art

Generally, sintered tungsten carbide base alloys have been produced by bonding tungsten carbide particles with cobalt as a metal binder.

Iron-bonded tungsten carbide composites tend to form a harmful double carbide of iron and tungsten (W_3Fe_3C) as the eta phase through the sintering process, and so the total carbon content of the compact is adjusted to preclude the formation of the eta phase W_3Fe_3C by adding a fixed carbon thereto. In the case of a carbon excess, the free carbon precipitates in the sintered tungsten carbide base alloy, which lowers the strength of the sintered tungsten carbide base alloy produced. Therefore, it is difficult to produce high strength and high toughness sintered tungsten carbide base alloys because of the very narrow permitted limit of carbon content in the iron-bonded tungsten carbide base alloys, and for this reason, some prior art exists directed toward improving this permitted limit of carbon content in iron-bonded tungsten carbide base alloys.

It is known that the very narrow permitted limit of carbon content in iron-bonded tungsten base alloys can be substantially improved by the substitution of nickel for a portion of the iron metal binder. Specifically, the carbon content can expand in accordance with the increase of the nickel content over about 4 weight percent in the iron-nickel alloys used as the metal binder. Tungsten carbide base alloys bonded with iron-nickel alloys, e.g., a Fe-25 Ni alloy, are already in commercial base (see R. Kohlermann et al., "Die Technik," vol. 11, 1957, pp. 736-746).

The primary object of this invention is to provide a high strength and high toughness steel-bonded tungsten carbide base composite having a bonding phase consisting essentially of an iron-nickel or an iron-nickel-cobalt alloy.

SUMMARY OF THE INVENTION

This invention provides a high strength and high toughness steel-bonded tungsten carbide base composite where-

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in molybdenum and/or chromium are employed as binder elements in conjunction with the iron-nickel or iron-nickel-cobalt alloys.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a phase diagram for binary alloys of iron and nickel;

FIG. 2 is a magnified phase diagram for binary alloys of iron and nickel;

FIGS. 3 to 10 are graphical representations of the effects on the plastic characteristics of the sintered tungsten carbide base alloys according to the present invention;

FIG. 11 is a photomicrograph of a sintered tungsten carbide base alloy specimen according to Example 1; and

FIG. 12 is a drawing of a testing condition.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Sintered tungsten carbide base alloys bonded with iron-nickel alloys undergo phase transformations by heating as shown in FIG. 1. The relationship between the cooling transformation and the heating transformation is as shown in FIG. 2. Specifically, referring to FIG. 2, a martensite transformation of a 75% Fe-25% Ni alloy occurs at about 150° C. during cooling; and on the other hand, an austenite transformation occurs at about 540° C. during heating. These phase transformations have an important influence upon the heat resistance of a tungsten carbide base alloy bonded with the above-identified 75 Fe-25 Ni alloy.

From the results which were obtained in a series of experiments, it was found that the bonded iron-nickel phase in a sintered tungsten carbide alloy shows remarkably different characteristics as compared with those of an iron-nickel alloy per se. For example, the saturation magnetization of a sintered 70 WC-30 (Fe-Ni) alloy, in accordance with various nickel contents, were determined as shown in FIG. 3. The saturation magnetization of the 70 WC-30 (Fe-Ni) alloy was increased remarkably by applying a sub-zero treatment to the 70 WC-30 (Fe-Ni) alloy in liquid nitrogen. Since it has been generally believed that the saturation magnetization is increased in proportion to the α -iron in the bonding phase; from the above fact, it may be concluded that the bonding phase contains a great deal of γ -iron therein. This conclusion is remarkably different as compared with the iron-nickel diagram as shown in FIGS. 1 and 2. Namely, from the facts described above, it may be concluded that in the iron-nickel alloy used as the bonding phase in a tungsten carbide alloy, the martensite transformation has been restrained by one cause or another. Because of the fact that the martensite reaction of an iron-nickel alloy is athermal, the one cause may be that the M_s (martensite transformation) temperature is lowered by the effects of the carbon and tungsten diffused in the bonding phase; while another possible cause may be that the martensite reaction is restrained by the effect of tungsten carbide particles surrounding the iron-nickel alloy used as the metal binder.

Accordingly, it is impossible to produce a WC-(Fe-Ni) alloy having a bonding phase of 100 percent martensite structure in an as-sintered condition. The saturation magnetization of a WC-(Fe-Ni) alloy may be effectively increased, under the sintered situation, by adding cobalt to the WC-(Fe-Ni) alloy as shown in FIG. 3, and generally, it is well known that the M_s temperature of iron-nickel alloys is elevated by adding cobalt to the alloy; and thus, this fact may be interpreted such that the remaining austenite in the bonding phase is reduced by the effect of the added cobalt.

On the basis of the results of the experiments described above, the present inventors have endeavored to examine the effects of adding certain elements to the iron-nickel alloy used as the metal binder. From the results of these experiments, it has been found that sintered tungsten carbide base alloys having a bonding phase consisting of iron-nickel alloys or iron-nickel-cobalt alloys and having added thereto molybdenum or molybdenum and chromium possess excellent properties.

One advantage is the improvement of the heat-resistance of the sintered tungsten carbide base alloy. The heat-softening resistances of various WC-(Fe-Ni) alloys, WC-(Fe-Ni-Co) alloys and tungsten carbide base alloys containing molybdenum and/or chromium as binder elements therein (after having applied thereto the aforementioned sub-zero treatment) are shown in FIG. 4 as the percent change in hardness after heating each alloy for one hour, wherein the hardness of each alloy before heating is presumed to be 100. As shown in FIG. 4, the alloys containing molybdenum therein according to the present invention had a superior heat-softening resistance as compared with the alloys having the bonding phases of only an iron-nickel or iron-nickel-cobalt alloy.

Various 70 WC-30 (Fe-16 Ni-10 Co) alloys containing various amounts of molybdenum and chromium were prepared in order to examine the effect of the added molybdenum and chromium. The composition of the respective bonding phases are shown in FIGS. 5 and 6. The transverse rupture strengths and hardnesses of the resulting alloys are shown in FIGS. 5 and 6, respectively, wherein the transverse rupture strength increases in accordance with increases in the molybdenum and chromium content; and especially, in the case of a molybdenum content of from 3 to 12 weight percent, a remarkable effect is recognized. The hardness also increases in accordance with an increase in the molybdenum content as shown in FIG. 6.

The minimum nickel content in the bonding phase of the tungsten carbide base alloys according to the present invention is about 4 weight percent as described above and the Ms temperature of the bonding phase decreases in accordance with the increase of nickel content, and thus the tungsten carbide base alloys according to the present invention, in the sintered condition have a large amount of austenite therein.

The relationship between the 0.2% yield stress of a WC-30 (Fe-Ni-Co-Mo-Cr) alloy and the martensite content therein is as shown in FIG. 7. The martensite content in the WC-30 (Fe-Ni-Co-Mo-Cr) alloy is varied by varying the nickel content therein or by heat-treating the alloy, the martensite content of the WC-30 (Fe-Ni-Co-Mo-Cr) alloys being determined by measuring the saturation magnetization values of the alloys. From the results shown in FIG. 7, it is clear that the 0.2% yield stress of the alloy increases in proportion with the increase of martensite content in the bonding phase of the alloy. Accordingly, the present inventors have concluded that to obtain a high strength steel-bonded tungsten carbide base alloy, a large amount of martensite has to be provided in the bonding phase of the alloy.

30 weight percent from the results of the experiments described above. It seems that the addition of cobalt to the metal binder improves the heat resistance of the iron-nickel bonded tungsten carbide base alloy, but the addition of cobalt over 25 weight percent to the metal binder reduces the strength of the resulting iron-nickel bonded tungsten carbide base alloy.

The stress-strain curves of a WC-30 (Fe-16 Ni-10 Co-4.7 Mo-2 Cr) alloy, according to the present invention, are shown in FIG. 8. Test pieces with a diameter of 4.5 mm. and a length of 9.0 mm. were employed in this compression test. The Instron universal testing machine was used in the compression test. The test pieces were subjected to the heat treatments as shown in Table 1.

TABLE 1

Legend for Fig. 8	Heat treating conditions	
	Annealing treatment	Aging treatment
B-1-----	As sintered-----	
B-2-----	850° C. for 30 minutes and oil quenched-----	200° C., 1 hour.
B-3, 3'-----	950° C. for 30 minutes and oil quenched-----	Do.
B-4-----	1,050° C. for 30 minutes and oil quenched-----	Do.

The variation of martensite content in the bonding phase of the alloys shown in FIG. 8 is shown in FIG. 9. The martensite content is determined by measuring the saturation magnetization value of the alloy. From the results shown in FIGS. 8 and 9, it will be understood that the martensite content in the bonding phase of steel-bonded tungsten carbide base alloys may be adjusted by heat-treating the steel-bonded tungsten carbide base alloy. The compressive strength of the steel-bonded tungsten carbide base alloy, having a bonding phase containing little martensite, is low; and on the other hand, the elongation of that alloy has a maximum value at about 30 weight percent of the primary martensite content in the bonding phase. The remaining austenite in the bonding phase may be converted to martensite by the strain-induced transformation during deformation as shown in FIG. 9.

From the facts described above, it may be concluded that the steel-bonded tungsten carbide base alloy must have a bonding phase consisting of the coexistent structures of martensite structure and austenite structure and the ratio between the martensite content and austenite content in the bonding phase can be adjusted by applying a heat-treatment to the steel-bonded tungsten carbide base alloy or by varying the nickel content in the bonding phase. Namely, the characteristics of the steel-bonded tungsten carbide alloy may be easily varied in accordance with the required use by applying a heat-treatment thereto or by varying the nickel content in the bonding phase.

The sintered tungsten carbide base alloys of the present invention are useful as punches or header-dies, where a requirement is a high toughness.

In order to compare the characteristics of the alloys of the present invention with those of standard alloys, the characteristics of the tungsten carbide alloys bonded with the steel binders containing molybdenum and/or chromium therein are shown in Table 2.

TABLE 2

Alloy No.	Matrix composition					Compressive strength, kg./mm. ²	0.2% proof stress, kg./mm. ²	Total strain, percent	Impact value, kg. m./cm. ²	TRS, kg./mm. ²	Hardness RA
	Ni	Co	Mo	Cr	Fe						
A-----	16.0	-----	-----	-----	Balance-----	390	203	>7.6	-----	284	82.0
B-----	16.0	-----	4.7	2.0	do-----	409	213	>7.6	-----	306	84.0
C-----	17.3	10.7	-----	-----	do-----	480	317	7.3	-----	235	86.1
D-----	16.0	10.0	4.7	2.0	do-----	503	332	7.2	1.10	340	87.0

The maximum nickel content in the bonding phase of the sintered tungsten carbide base alloy according to the present invention has been determined to be about

The characteristics of the commercial high speed steel and tungsten carbide-cobalt alloys are as shown in Table 3.

TABLE 3

Material	Compressive strength, kg./mm. ²	0.2% proof stress, kg./mm. ²	Total strain, percent	Impact value, kg. m./cm. ²	TRS, kg./mm. ²	Hardness RA
HSS(M2) ---	395	271	>8	1.16	320	83.5
WC-15Co ---	438	310	3.5	0.64	323	87.0
WC-25Co ---	299	188	8.4	0.89	307	83.8
WC-30Co ---	266	123	9.3	0.90	304	80.9

The alloys according to the present invention have superior properties of strength and toughness as compared with the commercial high speed steel and known tungsten carbide-cobalt alloys as shown in Tables 2 and 3.

The superior heat resistance properties which are one of the characteristics of the alloys according to the present invention allows these alloys to be serviceable as cutting tools and hot-working tools; and also, the heat softening resistance properties of these alloys, as shown in FIG. 4 allows the alloys to be serviceable as cold-working tools, such as punches and header dies.

In order to confirm the heat-resistance of the alloys of the present invention, cutting tests were performed under the following conditions:

Work material, S45C (steel, containing 0.45% C)

Side rake angle, 15°

Back rake angle, 6°

The cutting tools were prepared from a 12.7 mm. square of WC-30 (Fe-Ni-Co-Mo-Cr) alloys the binder phase compositions of which are shown in FIG. 10.

Cutting conditions:

(1) V=7.5 m./min.

d=1 mm.

f=0.10 mm./rev.

T=10°.

(2) V=32.5 m./min.

d=1 mm.

f=0.15 mm./rev.

T=10°.

The maximum wear widths of the clearance faces of the inserts were measured. The results of these measurements of maximum wear widths are shown in FIG. 10, wherein the results using cutting condition 2 are shown in parentheses (the values given for the respective binder phase compositions).

The temperature of the edge of the cutting tools during cutting was measured by the cutting tool-work thermocouple method, and the measured temperature of the edge of the WC-30 (Fe-16 Ni-10 Co) alloy tool was 200° C. during operation with cutting condition 1 and 400° C. with cutting condition 2.

Molybdenum exhibits a remarkable influence on the heat resistance of the alloys, chromium does not exhibit a remarkable influence on the heat resistance of the alloys, but chromium coexisting with molybdenum exhibits the influences as shown in FIG. 10.

The tungsten carbide base alloys according to the present invention can be manufactured by any well-known powder metallurgical process. The molybdenum and chromium in the alloy may be employed in the form of metallic molybdenum and chromium or as ferro-alloys thereof. When problems of oxidation occur, these elements may be added in the form of their carbides, such as Mo₂C and Cr₃C₂.

The basic carbides in the alloy according to the present invention may contain titanium carbide, vanadium carbide, hafnium carbide and/or other metal carbides in addition to tungsten carbide as the principal component. These additional carbides may be added only up to 30 weight percent of the tungsten carbide in the alloy because of their tendency of lowering the toughness of the alloy.

The bonding phase in the alloy of the present invention may be present in an amount of from 10 to 50 weight percent. In the case of a bonding phase deficiency, the characteristics as described above cannot be achieved, and in

the case of an excess of the bonding phase, the alloy cannot be produced effectively because of the deformation, through the sintering process, of the compact.

The present invention will be further illustrated by reference to the following non-limiting examples.

EXAMPLE 1

A mixture was prepared with the following composition:

	Wt. percent
WC powder	70.0
Carbonyl iron powder	20.2
Carbonyl nickel powder	4.8
Cobalt powder	3.0
Mo ₂ C	1.4
Cr ₃ C ₂	0.6
Carbon	0.45

Acetone was added and the mixture was subjected to wet milling in a ball mill for 72 hours and then compressed to a green compact under a pressure of 2 tons/cm.² after drying the mixture. The green compact was sintered in a vacuum atmosphere of 0.1–0.2 mm. Hg at 1400° C. for one hour. After cooling, the sintered body was cut and the surface wrapped using diamond paste and then etched with picric acid to produce a replica for the electron microscope. The electrophotography of the sintered body is shown in FIG. 11. In the microphotography, the lens-shaped patterns of martensite structure were observed in the bonding phase, and so it will be understood that the bonding phase of the sintered tungsten carbide base alloy according to the present invention comprises the coexistent structure of martensite structure and austenite structure.

The sintered tungsten carbide base alloy according to the present invention had mechanical properties as follows: a compressive strength of 503 kg./mm.²; a 0.2% yield point of 332 kg./mm.²; a total strain of 7.2%, a Charpy impact value of 1.10 kgm./cm.², the Charpy impact test being conducted employing specimens with a 4.5 mm. square and a 40 mm. span; a transverse rupture strength of 340 kg./mm.², the bending test being employed using a specimen with a 4 mm. thickness, a 8 mm. width and a 20 mm. span; and a RA hardness of 87.0.

The practical tests for this sintered tungsten carbide base alloy and the prior art high-speed steel were performed by a punch as shown in FIG. 12. In the results of these tests, the prior art high-speed steel was durable to work 500 pieces, but the sintered tungsten carbide base alloy according to the present invention was durable to work 45,000–50,000 pieces; that is, the sintered tungsten carbide base alloy according to the present invention was about 100 times as durable as compared with the prior art high-speed steel.

EXAMPLE 2

A mixture was prepared with the following composition:

	Wt. percent
WC powder	75
Carbonyl iron powder	16.8
Carbonyl nickel powder	4.0
Co powder	2.5
Mo ₂ C	1.2
Cr ₃ C ₂	0.5

A sintered tungsten carbide base alloy was produced from this mixture by the process as shown in Example 1.

The sintered tungsten carbide base alloy according to the present invention had the following mechanical properties: a compressive strength of 555 kg./mm.², a 0.2% yield point of 414 kg./mm.², a transverse rupture strength of 370 kg./mm.² and a RA hardness of 89.5.

A practical test for this sintered tungsten carbide alloy was performed by means of a cutting tool under the following conditions:

Rake angle: 30°

Work material: Ever-hard (trademark) which contains 0.25 to 0.35 wt. percent C, 0.21 wt. percent Cu, 1.48 wt. percent Mn and 0.14 wt. percent Mo and 0.24 wt. percent Si.

Cutting conditions:

V=10 m./min.

d=0.05 mm.

f=14 mm.

This sintered tungsten carbide tool cut the material 5 times as long as the prior art high-speed steel tool; and also a prior art hard metal tool could not cut the material because of a great deal of tipping of the edge of the tool.

EXAMPLE 3

The compositions and mechanical properties of the metal binders employed in Example 3 are as shown in Table 4.

TABLE 4

	Matrix composition				TRS, kg./mm. ²	Hardness RA
	Fe	Ni	Mo	Cr		
Present inven- tion.	Balance...	11.0	4.7	-----	301	87.0
	---do-----	11.0	4.7	2.0	288	85.3
	---do-----	16.0	4.7	2.0	306	84.7
Standard alloy...	Balance...	11.0	-----	-----	281	84.9
	---do-----	16.0	-----	-----	284	82.2

The present invention is not intended to be limited to the disclosure herein, and changes and modifications may be made in the disclosure by those skilled in the art without departing from the spirit and scope of the novel concepts considered to be within the purview and scope of this invention as defined by the appended claims.

What is claimed is:

1. A hard sintered tungsten carbide base composite consisting essentially of metal carbides containing tung-

sten carbide as the principal component and from 10 to 50 weight percent, based on the weight of the total composition, of a steel binder consisting essentially of steel containing from 4 to 30 weight percent nickel and optionally from 1 to 25 percent weight cobalt and from 1 to 15 weight percent molybdenum and optionally from 1 to 10 weight percent chromium.

2. The hard sintered tungsten carbide base composite according to claim 1, wherein the binder phase consists of a coexistent martensite and austenite structure.

3. The hard sintered tungsten carbide base composite according to claim 2, wherein the binder phase consists essentially of from 4 to 30 weight percent nickel, from 1 to 25 weight percent cobalt, and at least one member selected from the group consisting of from 1 to 15 weight percent molybdenum and from 1 to 10 weight percent chromium with the balance being substantially iron.

4. The hard sintered tungsten carbide base composite according to claim 3, wherein the metal carbide consists essentially of tungsten carbide only.

5. The hard sintered tungsten carbide base composite according to claim 4, wherein the binder phase consists essentially of from 4 to 25 weight percent nickel, from 1 to 20 percent cobalt, and at least one member selected from the group consisting of from 1 to 10 weight percent molybdenum and from 1 to 5 weight percent chromium with the balance being substantially iron.

6. The hard sintered tungsten carbide base composite according to claim 1 wherein said metal carbides contain at least 70 weight percent tungsten carbide.

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CARL D. QUARFORTH, Primary Examiner

R. E. SCHAFER, Assistant Examiner

U.S. Cl. X.R.

29—182.8; 148—126

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,746,519 Dated July 17, 1973

Inventor(s) Akio Hara, et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Figure 11 of the drawings shown on the attached sheet should be added to the grant only.

Signed and sealed this 26th day of February 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FIG. II

