

- [54] **NICKEL-BASE HEAT RESISTANT AND WEAR RESISTANT ALLOY**
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- [58] **Field of Search**..... 75/.5 BC, 203, 204, 122, 75/171; 29/182.7, 182.8; 148/32, 32.5
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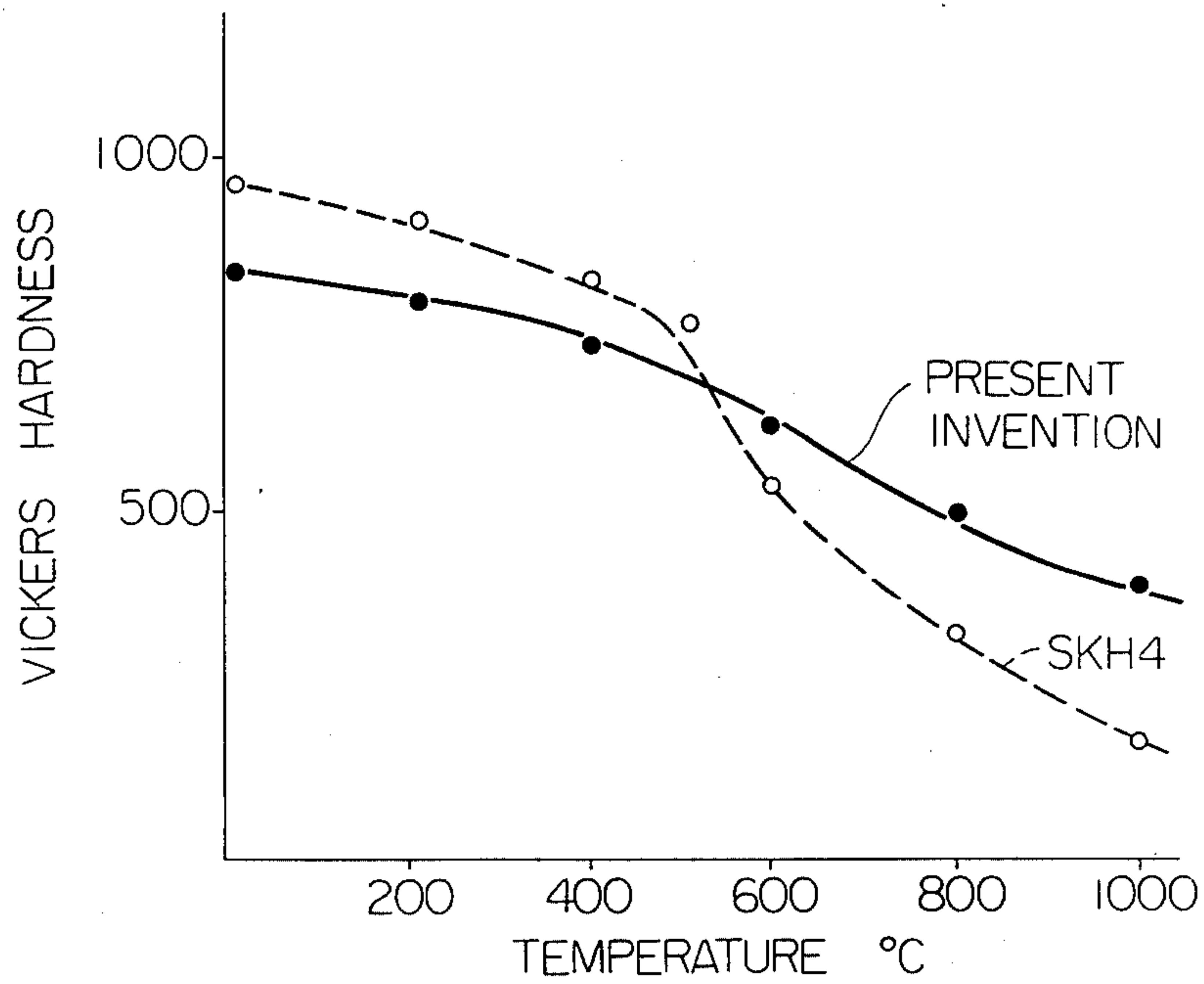
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[57] **ABSTRACT**

A heat resistant and wear resistant alloy of the carbide-dispersion and precipitation-hardening type, to be used for cutting tools, etc., has a basic composition consisting, in weight percent based on the total weight of said alloy, of from 10 to 90 percent dispersed particles composed of one or more kinds of carbides or composite carbides of transition metals from Groups 4a, 5a and 6a and the balance being from 70 to 90 percent Ni, from 2 to 10 percent Ti and 0.5 to 10 percent Al, and one or more kinds of alloy elements selected from the group consisting, in weight percent based on Ni-base matrix, of no more than 10 percent Ta, no more than 10 percent Nb, no more than 20 percent W and no more than 20 percent Mo.

**4 Claims, 1 Drawing Figure**



NOTE : COMPOSITION OF ALLOY OF THE PRESENT INVENTION : 20% (TiZr)C-10% MO<sub>2</sub>C-70%Ni BASE SUPER HEAD ALLOY (60% Ni-0.3% C-3% Ti-5.3% Al-13% Mo-5.3% Ta-13% W-0.01% Ce-0.09% Mg )

( COMPOSITION IN EXAMPLE 4 )



## NICKEL-BASE HEAT RESISTANT AND WEAR RESISTANT ALLOY

### RELATED APPLICATION

This application is related to application Ser. No. 441,123 filed Feb. 11, 1974.

The present invention relates to heat-resistant and wear-resistant alloys prepared by utilizing in combination the principles of dispersion strengthening due to the dispersion of carbide particles a Ni and of precipitation hardening through the formation of  $\gamma'$ -phase  $\{Ni_3Al(Ti)\}$  in a Ni-base matrix.

Alloys according to the present invention find their use as materials for cutting tools, wear-resisting tools for hot or cold working, etc. Accordingly, the alloys must have high strength and toughness at room temperature as well as at elevated temperatures, in addition to excellent anti-welding properties.

Hitherto, the materials used for cutting tools have been carbon tool steel, high speed steel, WC base-hard alloy, TiC base cermet, etc. Carbon tool steel and high speed steel are tough but the toughness tends to decrease sharply at temperature over about 600°C, so the tools made of such materials are used only in a low cutting range within which less heat is generated.

At increased cutting speeds, the WC base-hard alloys are best, although they suffer from such as being somewhat lower in anti-welding properties and in wear-resistance. Furthermore, the use of a tool made of such materials in the high speed cutting range gives rise to a demand for greater resistance to oxidation, because the cutting edge of a tool is subjected to a higher temperature than the rest of the tool. Therefore, within the high speed cutting range, TiC base cermet, which has excellent oxidation-resistance, finds a wide range of uses.

An alloy according to the present invention is provided as a sintered tool material, which contains one or more kinds of carbides of transition metals selected from the Groups 4a, 5a and 6a in the form of dispersion phase, and the balance of a composition of a Ni-base super-alloy, and is characterized in that the total amount of carbides or composite carbides is in the range from 10 to 90 percent, based on the total weight of said alloy and the balance thereof is a composition of Ni-base super alloy, in which is precipitated a  $\gamma'$ -phase  $\{Ni_3Al(Ti)\}$ .

The features of the alloy according to the present invention are that they retain the high strength and toughness obtained by containing in the Ni-base matrix high melting point metals, such as Ta, Nb, W, Mo, etc. and at the same time do not decrease in strength at a temperature up to 700°C to 800°C, due to the excellent heat-resistance of the matrix and the high strength of the precipitated  $\gamma'$ -phase at an elevated temperature. In addition, alloys of the present invention provide, in combination, excellent high resistance to wear and oxidation as a result of the carbide phases dispersed in the alloys.

As is clear from the forgoing, the alloys according to the present invention are superior in the properties required for tool materials and can be provided over a wide range of cutting modes, from light to heavy load, by controlling the carbide phase and the amount and nature of binder phase used; in addition they are superior in properties required for tool materials for cold or hot working tools.

Alloys according to the present invention provide excellent cutting characteristics, particularly in the low cutting speed range, in which high speed steel finds its principal application. High speed steel, in general, contains MC,  $M_6C$  and  $M_{23}C_6$  type carbides dispersed therein. The hardness of  $M_6C$  and  $M_{23}C_6$  type carbides does not go as high as 1,800 to 2,100 in terms of Vickers hardness. In contrast thereto, the hardness of the principal carbides of the present invention, such as for instance, TiC, goes as high as 3,000 to 3,200 (Vickers hardness). Also, they have good wettability to the matrix of Ni base super alloys as well as high oxidation resistance. The result is that the excellent properties of TiC are well reflected in the cutting performance of tools which contain it.

When the alloys of the present invention are used for cutting tools to be used in a low speed cutting range, the total amount of one or more kinds of carbides or composite carbides contained in the alloy should preferably be in the range of from 20 to 70 percent.

On the other hand, the Ni-base super alloy matrix functioning as a binding phase in the present invention has a basic composition consisting, in weight percent, of from 70 to 90 percent Ni, from 2 to 10 percent Ti and from 0.5 to 10 percent Al, said alloy further containing one or more kinds of alloy elements selected from the group consisting, in weight percent based on the total weight of the Ni-base matrix, of no more than 10 percent Ta, no more than 10 percent Nb, no more than 20 percent Mo and no more than 20 percent W.

In this respect, Ti and Al are essential as constituents for forming a  $\gamma'$ -phase  $\{Ni_3Al(Ti)\}$  which plays a major role in precipitation-hardening. If the amounts of Ti and Al are insufficient, less amount of the  $\gamma'$ -phase will be precipitated and the resulting alloy will have lowered heat-resistance. For this reason, a Ti content of at least 2 percent and an Al content at least 0.5 percent are necessary. However, if the contents of Ti and Al respectively exceed 10 percent, an undesirable brittle  $\eta$ -phase ( $Ni_3Ti$ ) or NiAl phase will be formed.

W, Mo, Ta and Nb each partially dissolve in a Ni-matrix, while partially forming carbides. These elements dissolved in a Ni-matrix effectively improve strength of an alloy at an elevated temperature. However, in case the amount of such elements is excessive, the toughness of the alloy will be decreased. Of these elements, Mo is best for improving the strength of boundaries of carbide particles and a binding phase, because the Mo added forms Mo-rich composite carbides surrounding the surface of a starting carbide, which exhibit good affinity to the Ni-base binding phase.

It may further contain one or more kinds of alloy elements selected from the group consisting, in weight percent based on the total weight of the Ni-base matrix, of no more than 1 percent Hf, no more than 0.5 percent Mg, no more than 1 percent in total, of rare earth elements (such as La, Y, Ce, etc.), and no more than 0.5 percent P.

A small amount of Mg, Hf, P and rare earth elements, if added, gives advantages such as improved deoxidation and desulfurization of the Ni-matrix, strengthening of grain boundaries and refining of crystal grains. However, if the amount of such elements added is excessive, the result is increased brittleness, because of the formation of compounds. Particularly, P easily forms phosphide with Ni, so that the amount of P should be limited to a very small amount.



Other than the elements above described, the addition, on the basis of the Ni-base matrix, of no more than 1 percent C, no more than 0.1 percent N, no more than 0.5 percent Cu, no more than 0.5 percent Re, no more than 0.5 percent Ba, no more than 0.5 percent Rh, or no more than 0.5 percent Be is effective. These elements may be added in place of the aforesaid small amount of elements or in combination therewith. When the amount of C, N, Be, Re, Cu, Rh, etc. added is very small, they dissolve in a Ni-matrix as solid solution, improving the strength of the matrix. However, if too much of such element is added, brittleness of the alloy increases.

When carbide dispersion, precipitation hardening type alloys of the present invention are used in a high speed cutting range, higher wear resistance and oxidation resistance are required, as compared with low speed cutting. To obtain these properties, a considerable amount of one or more kinds of carbides or composite carbides of transition metal from Groups 4a, 5a and 6a should be contained in the alloy. More specifically, the total weight of carbides or composite carbides contained in the alloy should be from 60 to 90 percent and dispersed in a binding phase of the alloy. In this respect, since  $\gamma'$ -phase is precipitated in the binding phase, the strength of the alloy at elevated temperatures will be much improved, as compared with the case where precipitated particles are not contained in the binding phase. More particularly, when comparing the conventional alloy with those of the present invention in terms of the use of the same amount of binder phase, those according to the present invention are much harder at an elevated temperature, so that wear resistance during continuous cutting is improved. Suppose that the wear resistance of a level the same as that of the conventional alloy is desired; then the amount of binder phase may be increased, thereby providing more improved intermittent cutting capability.

Tools which are employed as hot compression dies, hot extrusion punches, hot drawing dies, hot working rolls, hot forging dies, etc. for hot working are subjected to a high temperature for a relatively long period of time. Therefore, in addition to the usual resistance against wear and impact, and creep resisting and anti-welding properties, they must be hard enough to resist softening and deformation at the elevated temperature due to the temperature rise during service. For such applications, there are among the alloys according to the present invention sintered tool materials of Ni-base super alloys containing from 10 to 60 percent by weight of one or more kinds of carbides or composite carbides of transition metals from Groups 4a, 5a and 6a in the form of dispersion phase and the balance of a composition of a Ni-base super alloy. The prior art tool steels and high speed steel which have been widely used tend to soften at a temperature of above 600°C and thus are not usable, and in addition such tools present insufficient anti-welding properties.

According to alloys of the present invention, the temperature at which softening starts may be increased to 800°C, because the strength of the binding phase at an elevated temperature is improved due to the precipitation of a  $\gamma'$ -phase. Furthermore, alloys according to the present invention provide the characteristics required in tool materials for hot working, due to the excellent wear resistance and anti-welding properties provided by the carbide particles.

The accompanying graph shows hardness at elevated temperatures of alloy of the present invention in comparison with high speed steel (JIS-SKH 4).

The following examples are illustrative of several aspects of the present invention. Unless otherwise indicated, the percentage given for alloying elements is weight percent based on total weight of alloy.

#### EXAMPLE 1

The following were added to 30 percent TiC, and 10 percent (WTi)C, each being of  $1\mu$  in size: 50 percent Ni, 5 percent NiAl (Ni : Al = 7 : 3), 2 percent Ti and 3 percent Mo. The mixture thus prepared was wet-mixed, dried, compacted, sintered under vacuum at 1,350°C for 1.0 hour. The sintered product was cooled in the furnace to the temperature of 1,150°C then oil-quenched, and tempered at 760°C for 4.0 hours. The hardness of the alloy thus obtained was, on the Rockwell C scale, 59 after oil-quenching, and 62 after tempering respectively. The transverse rupture strength thereof was 220 kg/mm<sup>2</sup>.

#### EXAMPLE 2

10 percent WC of a size of  $1\mu$  was added to 20 percent TiC powder of  $3\mu$  in size which had been obtained by crushing commercially available TiC of minus 100 mesh in a wet type ball mill. Then, the following were added to this TiC-WC mixture: 50 percent Ni, 10 percent NiAl (Ni : Al = 7 : 3), 2.04 percent Ti, 7.9 percent Mo, 0.05 percent Cu and 0.01 P. These added powdery elements forms a binding phase for the carbide particles. The powder mixture thus prepared was wet-mixed, compacted, sintered under vacuum of  $10^{-1}$  mmHg at 1,350°C for 10 hours. The sintered product was subjected to solution treatment at 1,150°C for 4 hours and thereafter to aging treatment at 750°C for 4 hours.

The hardness of the alloy thus obtained was 63 R<sub>C</sub> (on the Rockwell hardness C scale). The cutting test results of such alloys are shown in Table 1.

Table 1

Cutting conditions:				
Work Material	AISI 4340			
Feed	0.3 mm/rev.			
Depth of Cut	1.5 mm			
Cutting time	20 minutes			
	Flank Wear (mm)			
	Speed (m/min.)	20	50	60
Sample this invention		0.05	0.09	0.12
SKH 4		0.2	0.6	1.0

#### EXAMPLE 3

The following were added to 15 percent (TiTa)C, 5 percent WC and 5 percent Mo<sub>2</sub>C each being of  $2\mu$  in size: 45 percent Ni, 10 percent NiAl (Ni : Al = 7 : 3), 4 percent Ti, 0.05 percent Re, 0.5 percent Hf, 0.01 percent P. The powder mixture thus prepared was then wet-mixed in a ball mill, vacuum-dried, compacted under a pressure of 1 t/cm<sup>2</sup>, held under vacuum of  $10^{-2}$  mmHg for 10 hours at 1,330°C, cooled down to 1,000°C at a cooling rate of 5°C/min., and then cooled to room temperature at a cooling rate of 10°C/min. The hardness of the alloy thus obtained was 61 R<sub>C</sub>.



## EXAMPLE 4

The following were added to 20 percent (TiZr)C and 10 percent Mo<sub>2</sub>C each being of 1 $\mu$  in size: a Ni-base super alloy powder consisting of 60 percent Ni, 0.3 percent C, 3 percent Ti, 5.3 percent Al, 13 percent Mo, 5.3 percent Ta, 13 percent W, 0.01 percent Ce and 0.09 percent Mg. The powder thus obtained was wet-mixed, compacted under a pressure of 1 t/cm<sup>2</sup>, sintered under vacuum of 10<sup>-1</sup> mmHg at 1,320°C for 1.0 hour, then subjected to solution treatment under vacuum at 1,150°C for 4 hours, oil-quenched, tempered at 800°C for 2 hours. The hardness of the alloy thus obtained was 64 R<sub>C</sub> and the transverse rupture strength was 170 kg/mm<sup>2</sup>. The hardness, at elevated temperatures, of the alloys according to the present invention, in comparison with SKH 4 is shown in FIG. 1, which reveals that the hardness of the alloys of the present invention is excellent at a temperature range above 600°C.

The chemical composition of SKH 4 comprises 0.70–0.85 percent C, no more than 0.40 percent Si, no more than 0.40 percent Mn, no more than 0.030 percent P, no more than 0.030 percent S, 3.80–4.5 percent Cr, 17–19 percent W, 1.0–1.5 percent V, 9.0–11.0 percent Co and the rest iron.

## EXAMPLE 5

The following were added to 30 percent WC and 10 percent TaC each being of 1 $\mu$  in size: 36.5 percent Ni, 10 percent NiAl (Ni : Al = 7 : 3), 3 percent Ti, 10 percent Mo, and 0.5 percent C. The powder thus prepared was compacted and sintered under vacuum of 10<sup>-1</sup> mmHg at 1,380°C for 1 hour, subjected to solution treatment under vacuum at 1120°C for 4 hours and tempered at 800°C for 4 hours. The hardness of the alloy thus obtained was about 69 R<sub>C</sub>, and the transverse rupture strength thereof was 170 kg/mm<sup>2</sup>.

## EXAMPLE 6

The following were added to 60 percent TiC of 3 $\mu$  in size, 10 percent NbC of 3 $\mu$  in size and 5 percent VC of 1 $\mu$  in size: 16 percent Ni, 4.5 percent NiAl (Ni : Al = 7 : 3), 1.5 percent Ti, 1.3 percent Mo, 1.6 percent W and 0.1 percent C. The powder thus prepared was wet-mixed, compacted under a pressure of 1 t/cm<sup>2</sup>, sintered under vacuum of 10<sup>-2</sup> mmHg at 1,120°C for 4 hours, oil-quenched, and tempered at 800°C for 2 hours. The hardness of the alloy thus obtained was 91.5 R<sub>A</sub> (on the Rockwell hardness A scale). The transverse rupture strength thereof was 140 kg/mm<sup>2</sup>.

Table 2 shows the cutting test results for tools according to the present invention as well as the conventional tools in terms of the use of the binding phase of the same amount. The alloys of the present invention exhibit excellent wear resistance.

Table 2

Cutting conditions:		
Work Material	AISI 4340	
Feed	0.45 mm/rev.	
Depth of Cut	1.5 mm	
Cutting time	5 minutes	
	Flank Wear (mm)	
Speed (m/min.)	150	200
Sample		
this invention	0.05	0.09
conventional alloy	0.1	0.16

## EXAMPLE 7

The following were added to 75 percent TiC powder of 1 $\mu$  in size: 2 percent Ti, 15 percent Ni, 4.9 percent NiAl (Ni : Al = 7 : 3), 3 percent Mo and 0.1 percent Hf. The powder thus prepared was mixed, compacted, sintered and heat-treated in the same manner as in Example 3. The hardness of the alloy thus obtained was 92 R<sub>A</sub>. The transverse rupture strength thereof was 160 kg/mm<sup>2</sup>.

## EXAMPLE 8

The following were added to 50 percent (TiMo)C, 20 percent WC and 5 percent TaC each being of 1 $\mu$  in size: 2 percent Ti, 16.89 percent Ni, 3 percent NiAl (Ni : Al = 7 : 3), 1 percent Mo, 2 percent W, 0.1 percent C and 0.01 percent Mg. The powder thus prepared was mixed, compacted, sintered under vacuum at 1,370°C for 1.0 hour, subjected to solution treatment at 1,200°C for 4 hours, oil-quenched, tempered at 800°C for 2 hours. The hardness of the alloy thus obtained was 91 R<sub>A</sub>. The transverse rupture strength thereof was 160 kg/mm<sup>2</sup>.

## EXAMPLE 9

The following were added to 30 percent WC of 1 $\mu$  in size, 10 percent TiC of 3 $\mu$  in size and 6 percent Cr<sub>3</sub>C<sub>2</sub> of 3 $\mu$  in size: 36.2 percent Ni, 2.7 percent Ti, 5.4 percent NiAl (Ni : Al = 7 : 3), 5 percent W, 4.5 percent Ta, and 0.2 percent C. The powder thus prepared was mixed, compacted, sintered under vacuum at 1300°C for 1.0 hour, subjected to solution treatment at 1200°C for 4 hours, oil-quenched, tempered at 800°C for 2 hours. The hardness of the alloy thus obtained was 55 R<sub>C</sub>. The transverse rupture strength thereof was 150 kg/mm<sup>2</sup>.

## EXAMPLE 10

The following were added to 20 percent (TiZr)C, 5 percent WC and 5 percent Mo<sub>2</sub>C each being of 1 $\mu$  in size: the 70 percent Ni-base super alloy powder consisting of 75 percent Ni, 4 percent Ti, 5 percent Al, 7 percent Mo, 2 percent Ta, 0.1 percent Ce, 0.1 percent Be and 6.8 percent W. The powder thus prepared was mechanically mixed, then dried, compacted, sintered under vacuum of 10<sup>-2</sup> mmHg at 1,320°C for 1.0 hour, then subjected to solution treatment at 1,120°C for 4 hours under vacuum and tempered at 800°C for 4 hours. The hardness of the alloy thus obtained was 58 on the Rockwell C scale. The transverse rupture strength thereof was 240 kg/mm<sup>2</sup>.

The cutting test results are shown in Table 3.

Table 3

Cutting conditions:		
Work Material	AISI 4340	
Feed	0.42 mm/rev.	
Depth of Cut	1.0 mm	
Cutting time	20 minutes	
Cutting speed	45 m/min.	
Sample	Flank Wear	Remark
this invention	0.25 mm	less welding
SKH 4	1.5 mm	excessive welding

## EXAMPLE 11

The following were added to 40 percent WC of 3 $\mu$  in size and 10 percent (WTi)C of 1 $\mu$  in size: 37 percent

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Ni, 5 percent NiAl (Ni : Al = 7 : 3), 2.9 percent Ti, 1 percent Ta and 0.1 percent Mg. The powder thus prepared was mixed, compacted and sintered under vacuum of 10<sup>-2</sup> mmHg at 1400°C for 1.0 hour, then subjected to solution treatment under vacuum at 1,120°C for 4 hours, oil-quenched, and tempered at 800°C for 4 hours. The hardness of the alloy thus obtained was as high as 74 (on the Rockwell C scale). The transverse rupture strength thereof was 220 kg/mm<sup>2</sup>.

What is claimed is:

1. A powder metallurgy sintered alloy having a basic composition consisting essentially of, in weight percent based on the total weight of said alloy, from 10 to 90% of substantially uniformly dispersed preformed particles composed of at least one carbide or composite carbide of transition metals of Groups 4a, 5a and 6a and the balance a nickel base matrix consisting essentially of from 70 to 90 percent Ni, from 2 to 10 percent Ti, from 0.5 to 10 percent Al, and at least one alloy element, in an amount sufficient to impart high temperature strength, selected from the group consisting of up

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to 10 percent Ta, up to 10 percent Nb, up to 20 percent W and up to 20 percent Mo.

2. An alloy as defined in claim 1, wherein said alloy contains at least one alloy element selected from the group consisting, in weight percent based on the Ni-base matrix, of up to 1 percent Hf, up to 0.5 percent Mg, up to 1 percent, in total, of rare earth elements, and up to 0.5 percent P.

3. An alloy as defined in claim 1, wherein said alloy further contains at least one alloy element selected from the group consisting, in weight percent based on the Ni-base matrix, of up to 1.0 percent C, up to 0.1 percent N, up to 0.5 percent Cu, up to 0.5 percent Re, up to 0.5 percent Ba, up to 0.5 percent Rh and up to 0.5 percent Be.

4. An alloy as defined in claim 3, wherein said alloy further contains at least alloy element selected from the group consisting, in weight percent based on the Ni-base matrix, of up to 1 percent Hf, up to 0.5 percent Mg, up to 1.0 percent, in total, of rare earth elements and up to 0.5 percent P.

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