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(54) **ARTICLE AYANT UN REVETEMENT RESISTANT A L'USURE ET METHODE DE REVETEMENT CONNEXE**

(54) **ARTICLE WITH WEAR RESISTANT COATING AND METHOD**

(57) An article having a wear and corrosion resistant coating is formed by blending a powder formulation having a metal carbide-metal binder component and a nickel base boron containing alloy component, depositing the blend on the body of the article by a method capable of producing a coating with an as-deposited porosity of less than 5% and a boron content of 1.3 to 3.0 wt % of the whole coating, and heat-treating the coated article to achieve in the coating a microhardness above 900 kg/mm^2 HV.3 and the elimination of all interconnected porosity. The coating will sustain oil quenching without cracking.

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ARTICLE WITH WEAR RESISTANT COATING AND METHOD

Abstract of the Invention

An article having a wear and corrosion resistant coating is formed by blending a powder formulation having a metal carbide-metal binder component and a nickel base boron containing alloy component, depositing the blend on the body of the article by a method capable of producing a coating with an as-deposited porosity of less than 5% and a boron content of 1.3 to 3.0 wt % of the whole coating, and heat-treating the coated article to achieve in the coating a microhardness above 900 kg/mm^2 HV.3 and the elimination of all interconnected porosity. The coating will sustain oil quenching without cracking.

ARTICLE WITH WEAR RESISTANT COATING AND METHOD

Field of the Invention

This invention relates to an article having a wear and corrosion-resistant coating and a method for forming a wear and corrosion resistant coating on a substrate in which the coating will not crack when quenched in oil along with its substrate.

Background of the Invention

It is known to form a wear and corrosion resistant coating on a metallic substrate by depositing at least one coating of a metal carbide and binder, particularly tungsten carbide and cobalt and a nickel based alloy using a plasma, detonation gun or other thermal spray technique followed by a heat treatment operation. This method is described in detail in U.S. Patent 4,173,685 issued to M. H. Weatherly on November 6, 1979. The coating, as taught in the Weatherly patent, may be formed by depositing two successive layers (the two layer method) on a metallic substrate followed by heat treatment or by depositing a single layer (the one-layer method) followed by heat treatment. In the two layer method a metal carbide layer is initially formed on the metallic surface preferably using a detonation gun followed by the deposition of a nickel based alloy or mixture of alloys containing boron. The range of boron in the second layer for the two layer method should be between 3 and 18 wt% when the density of the first layer is above 95% theoretical and between 6 and 18 wt% when the density of the first layer is between 75 and 95% of theoretical. In the one layer method a metal carbide powder containing a metal binder such as cobalt and a nickel based alloy or mixture of alloys is mixed and deposited as one layer. The content of the

metal carbide and binder is between 40 wt. % and 75 wt. % of the total composition and the boron content of the nickel based alloy or mixture of alloys is above 6 wt %. Although suitable wear resistant coatings may be formed in accordance with the teaching of the aforementioned Weatherly patent on a wide variety of steel substrates it is not recommended for use on steels that have to be hardened by oil quenching from elevated temperatures and then optionally tempered to achieve useful strengths and mechanical properties. If hardened before coating, such steels will be annealed by the heat treatment that is required in the aforementioned Weatherly process to develop the optimum wear and corrosion-resistant properties of the coating (hereinafter referred to as the "Weatherly Coating"). After the Weatherly coating has been heat-treated it will crack if subjected to reheating and oil-quenching to develop the most useful properties of the steel.

Summary of the Invention

A method was discovered in accordance with the present invention for forming an article composed of a body and a superimposed coating that exhibits high wear and corrosion resistance after heat treatment, and has a porosity of less than 5%. This coating may be used on any body but is especially intended for use on steel bodies that require heat treatment and oil-quenching after coating because it will not crack when quenched into oil from a high temperature.

The article of the present invention comprises a body and a superimposed coating with said coating having less than 5% porosity and a composition consisting essentially of a metal carbide-binder fraction comprising one or more metal carbides selected from the class of metal carbides consisting of

tungsten, chromium, vanadium, hafnium, titanium, zirconium, niobium, molybdenum and tantalum carbides and compounds thereof along with a metal binder selected from the class consisting of Co, Ni, Fe and alloys thereof, and a fraction comprising a nickel-based boron-containing alloy of such composition that boron constitutes 1.3 to 3 wt % of the coating.

The method of the present invention for coating a body to form a wear and corrosion resistant surface coating comprises the steps of: preparing a powder composition consisting essentially of a metal carbide-binder fraction consisting of at least one metal carbide selected from the class of metal carbides consisting of tungsten, chromium, vanadium, hafnium, titanium, zirconium, niobium, molybdenum and tantalum carbides and compounds thereof along with a metal binder selected from the class consisting of cobalt, nickel, iron and alloys thereof and a fraction consisting of a nickel-based boron containing alloy having a boron content such that, upon deposition by a method capable of producing a coating with less than 5% included porosity, the boron content of the coating lies in the range of 1.3 to 3 wt% of the total coating composition, and depositing said powder composition by said method.

Brief Description of the Drawings

The following detailed description of the invention should be read in conjunction with the accompanying single Figure showing the relationship between the metal carbide-metal binder component and the boron content of the nickel-based alloy in the powder formulation.

Detailed Description of the Invention

The powder composition of the present invention includes a metal carbide-binder fraction comprising tungsten, chromium, vanadium, hafnium, titanium, zirconium, niobium, molybdenum or tantalum carbide or mixtures or compounds thereof and up to 25 wt % of a metal binder such as Co, Ni and Fe and a fraction comprising a nickel-based alloy containing boron. The preferred metal carbide is tungsten carbide and the preferred metal binder is cobalt in a range of preferably between above 0 and 15 wt %.

The powder formulation must be applied to the body by a method, preferably a thermal spray process, capable of producing a coating with less than 5% included porosity. The nickel alloy fraction of the powder mix must have a boron content such that, upon deposition by such method capable of producing a coating with less than 5% porosity, the boron content of the coating lies in the range of 1.3 to 3.0 wt% of the total coating composition. Commercial thermal spray processes which may be used to provide the required high density coating include the detonation gun, hypersonic combustion or high velocity oxy-fuel spray coating processes and other "high velocity" spray coating processes. The detonation gun process is the preferred process and is well known and fully described in U.S. Patent No. 2,714,563, 4,173,685 and 4,519,840, respectively. In the detonation gun process oxygen, acetylene and nitrogen are fed into a gun barrel along with the charge of material being coated and ignited. The resultant detonation wave accelerates the powder while heating it close to or above its melting point. When the powder formulation is applied to the body using the detonation gun technique, it is most advantageous if the nickel-alloy fraction of the powder

mix has a boron content such that the boron content of the total powder mix is between 1.0 and 2.7 wt%.

It is crucial to the present invention that the as-deposited coating have a porosity of less than 5%. The powder composition of the present invention when deposited with this low porosity using an appropriate thermal spray process and subjected to a heat treatment at above 950°C (hereinafter referred to as the "primary heat treatment") forms a hard, ductile, impervious coating that is able to survive, without cracking, oil-quenching from above 800°C. During the primary heat treatment, the porosity will reduce to 0 to 90% of its as-coated value and the original powder components will convert to a mixture of carbides and borides dispersed in a nickel alloy matrix. After primary heat treatment,a coating with the specified as-deposited composition and density will exhibit a hardness of greater than 900kg/mm^2 when measured by the Vickers method with 300 gram load and will exhibit a total porosity of less than 5%, preferably less than 2%, with no through porosity, i.e. any voids are closed.

The coating resulting from the primary heat treatment has excellent wear and corrosion resistance and no further processing is needed to take advantage of these properties, though the coating may be ground or otherwise finished to favorably modify its surface characteristics. In addition, the primary heat treatment may be followed by a secondary heat treatment designed to modify the mechanical properties of the supporting body without detriment to the coating. This heat treatment may be, for example, an aging heat treatment or an oil-quenching treatment appropriate to the substrate. A third heat treatment, to temper the quenched steel, as is common practice in heat treating, may also be applied without detriment to the coating.

Each heat treatment may be carried out in a vacuum or in an appropriate atmosphere. The secondary heat treatment may be carried out as a continuation of the primary heat treatment or separately from the primary heat treatment. In fact, the coating can be cooled and reheated and then quenched.

A relationship exists in the coating composition between the metal carbide-metal binder component and the boron content of the nickel-based alloy which in concert with the method of application must be satisfied to produce acceptable coating characteristics in terms of high stress abrasive wear resistance, low porosity and ability to sustain oil quenching without cracking. Typically the interdependence between the metal carbide-metal binder and the nickel based alloy is shown in Figure 1 using a composition of a WC-CO powder containing 4.4%C, 9.4%Co, 0.6%Fe, balance W and a Ni-B alloy which is composed of a combination of two nickel-based alloy components identified as Ni-B alloy 1 and Ni-B alloy 2, respectively. The nominal composition of Ni-B alloy 1 is: 14 wt % B, 2 wt. % Fe, balance Ni, and the nominal composition of the Ni-B alloy 2 is: 3% B, 3% Fe, 4% Si, 7% Cr, balance Ni. In Figure 1, the ordinate represents the percentage of the WC-Co powder in the powder mix and the abscissa the percentage of Ni-B alloy 1. The proportions of Ni-B alloy I and Ni-B alloy 2 control the boron content of the powder formulation. The circled data points in Figure 1 define the boundaries of a triangular-like geometry and correspond to the data identified in the following Tables I and II respectively. In Table I, the boron content of each of the mixtures is specified as the percentage of boron in the combined Ni-B alloy independent of the wt. % of the metal carbide. Table II shows the weight percent of boron in the powder and

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coating from which it should be noted that the boron content in the coating is not only retained but is enhanced from that in the powder

Table I

--Mix Composition-- wt. percent			
WC-Co	Ni-B Alloy 1	Ni-B Alloy 2	% B in Ni-B Alloys
75.0	6.0	19.0	5.64
65.0	6.0	29.0	4.88
50.0	6.0	44.0	4.32
71.0	5.0	24.0	4.90
65.0	5.0	30.0	4.57
57.0	5.0	38.0	4.28
67.0	4.0	29.0	4.33
65.0	4.0	31.0	4.26
63.0	4.0	33.0	4.19
65.0	3.6	31.4	4.13

Table II

--Powder Mix Comp-- wt. percent				
			Percent Boron	
WC-Co	Ni-B Alloy 1	Ni-B Alloy 2	In Pwdr	In Ctng
75	6.0	19.0	1.4	1.9
65	6.0	29.0	1.7	2.2
50	6.0	44.0	2.2	2.6
71	5.0	24.0	1.4	1.8
65	5.0	30.0	1.6	2.0
57	5.0	38.0	1.9	2.3
67	4.0	29.0	1.5	1.9
65	4.0	31.0	1.5	1.9
63	4.0	33.0	1.6	2.0
65	3.6	31.4	1.5	1.9

The area within the triangle formed in Figure 1 delineates the range of powder compositions which will form a coating having properties of high wear resistance, low porosity and the ability to withstand

oil quenching without cracking. The optimum boron content range is between 4 wt. % and 5 wt. %. A boron content of above 6 wt % in the nickel boron alloy powder formulation results in a coating which cracks when quenched in oil. The range of the metal carbide-metal binder is also limited to between 50 and 75 wt % of the total mixture and preferably between 55 and 65 wt The percent of boron must be correlated to the percent of the metal carbide-metal binder to remain within the triangular region. The region above line A-B of Figure 1 designates a region of high wear resistance and a microhardness above 900 HV.3, whereas in the region above line A-C the porosity will be too high and the coating will exhibit interconnected porosity. The content of boron in the coating should be between 1.8 and 2.6 wt % in the case exemplified in figure 1 and between about 1.3 to 3.0 wt % in the most general case. When deposition of the coating is done by means of a detonation gun, as is assumed in Tables 1 and 2 and figure 1, the content of the metal carbide and binder must lie between 40 and 65 wt % and the percent of boron in the powder between 1.4 and 2.2 wt %. The article of the present invention is particularly suitable for high stress abrasive wear environments such as, for example, a steel guide or work roll. The coating formed in accordance with the present invention is particularly suitable as a bearing surface for any type of bearing and for use in providing a surface coating for a valve seat or valve gate.

The following are examples which illustrate the invention and its advantage over the prior art:

Example I

A powder mix (Powder Mix 1) was prepared of a WC-Co powder containing 86% W, 9.5% Co, 4.5% C with an

alloy containing 83% Ni, 14% B, 2% Fe (Ni-B Alloy 1) and another alloy containing 83% Ni, 3% B, 7% Cr, 4% si, 3% Fe (Ni-B Alloy 2) in such proportions as to net 1.7% B in the mix. Powder Mix 1 was deposited by means of a detonation gun onto 1/2" x 3/4" x 2.711 blocks of AISI 1018 steel. This detonation gun coating exhibited an as-deposited porosity of less than 5%. The resultant coating (Coating 11) had a microhardness greater than 900 HV.3 and a porosity of less than 1% after primary heat treatment to a temperature in excess of 1000°C. A coating made on a similar block of AISI 1018 steel using the same powder through a plasma torch was less than 95% dense though otherwise appearing to be of high quality in the as-deposited state, but was found to contain more than 10% porosity after primary heat treatment and its microhardness could not be measured accurately because of the high porosity. When deposited on the large faces of a 111 x 31, x 611 4140 steel block later heated to over 1000°C for 1 hr and subsequently reheated to 850°C and quenched in oil, Coating #1 did not crack. The plasma torch coating could not be oil quenched without cracking.

Example II

It is an essential part of the concept of the present invention that the boron be retained in the coating at specific levels throughout the deposition and heat treatment. Coating #1 was deposited onto a 211 diameter, 611 long aluminum tube from which it was broken off by crushing the tube. The chemical composition of this coating was determined by standard methods of chemical analysis. Essentially identical results were obtained when the coating was deposited on a flat plate made of low carbon steel and again broken off mechanically. Coating #1 is made from Powder Mix

1, which contains 1.7% boron, but when removed from the substrate and analyzed it was found to contain 2.1% B. The apparent increase in B content is a result of preferential loss of other constituents during coating. In contrast, a coating made by the spray and fuse process from Stellite* SF6 powder, which also contains 1.7% B, was found by analysis to contain only 1.2% B.

Example III

A 511 O.D., 3/4" wall tube made of AISI 4140 steel was coated with 0.01611 of Coating #1 and primary heat-treated, then subsequently reheated to 850°C, oil quenched and tempered. The coating did not crack.

Example IV

Flat plates, 1.211 x 311 x 811, of AISI 4130 steel were coated on the two large faces with 0.01411 - 0.01611 of Coating #1 and then subjected to the primary heat-treatment for the coating. Following this, they were oil quenched and tempered to harden the substrate to 40 HRC at the surface (20 HRC at the center). Fluorescent penetrant inspection of the coatings revealed no cracking.

Example V

The foregoing experiment was repeated on two plates of similar size made of AISI 4140 steel and on a valve gate, 4" x 7" x 1.8" made of AISI 4130 steel. No cracking of the coating was observed subsequent to oil quenching and tempering of any of these.

Example VI

A tube of AISI 52100 steel, 211 in outside diameter x 611 long, with a 1/8" wall thickness, coated with 0.01211 of Coating #1 and put through the usual

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successive heat treatments also survived oil quenching without the coating cracking.

Example VII

Coating #1 was applied to the O.D. of a centrifugally cast steel mill work roll of nominal composition 1.7% C, 1.5% Ni, 1.1% Cr, 0.5% Mo, balance Fe and impurities and given the primary heat-treatment for the coating, but no secondary heat treatment. It is inherent in the operation of such rolls that each area of the surface is alternately heated and quenched as it moves into and out of contact with the hot steel. The coating was then ground and the roll installed in the finishing station of an I-beam shaping line. Three hundred tons of product was successfully rolled before the coating was penetrated. Penetration occurred in an area where the grinding had substantially reduced the coating thickness as a result of some out-of-roundness that developed during heat-treatment. It was evident from inspection of the coating on the remainder of the roll that the coating had survived numerous impacts by the leading edges of the beams that were being shaped. Moreover, furrows observed in the coating indicated that significant drag had developed between the coating and the I-beam at times during rolling, but the coating had neither cracked nor delaminated. It was also observed that neither the coating nor the substrate exposed by penetration of the coating exhibited the typical thermal fatigue patterns (firecracking) that usually degrade these rolls. The Weatherly coating, when applied to this substrate, blistered and cracked during primary heat treatment.

Example VIII

Spray and fuse coatings were prepared by an

outside source from Stellite SF6 powder and from Stellcar Composite 1 powder. The composition of the former is nominally 1.7% B, 19% Cr, 13.5% Ni, 7.5% W, 2.3% Si, 3% Fe, balance Co; Stellcar Composite 1 is a mix of 60% WC and 40% of a Ni-base alloy. Both are standard commercial spray and fuse coatings. These coatings as supplied to us by a commercial vendor on 111 x 311 x 611 blocks of 4140 steel, were much more porous than coatings of the subject invention. By examination of mounted cross sections the porosity of the Stellcar* Composite 1 coating was estimated as being 15 - 25 percent, while that of the Stellite SF6 coating was 6 8 percent. When subjected to oil quenching on 311 x 611 x 111 blocks of 4140 steel, the Stellite SF6 coating developed cracks just under the surface running parallel to the surface. The Composite 1 coating developed numerous cracks that ran completely through the coating from the surface to the substrate. While the cracking of the Stellite SF6 coating was relatively minor, it should be noted that this coating is significantly lower in hardness than the coatings of this invention, measuring only 450-500 HV.3.

Example IX

Samples of Coating #1 were prepared by coating Powder Mix 1 onto low carbon steel substrates for wear rate and mechanical property determinations and then tested in parallel with similarly prepared specimens coated using a plasma torch with a coating composition as taught in Weatherly containing tungsten carbide-cobalt and a nickel based alloy with about 8.5 wt% B and having about 3.4 wt% B in the coating. The results of these wear measurements are shown in Table III as indicated below where it is evident that the two coatings are essentially equivalent in the properties

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tested. The Weatherly coating, however, cracked when quenched in oil on pieces of the same size, shape, and composition as those on which Coating #1 survived.

Table III

Test	Coating of Invention	Weatherly Coating
High Stress Abrasion (a)	3.9	3.2 - 5.0
300 Erosion (A'203) (b)	19	19 - 25
900 Erosion (A'203) (b)	85	90 - 95
Sand Abrasion (c)	1.7 - 1.8	1.3 - 2.0

(a) mil/min
(b) μmlg
(c) mm^3/1000 revolutions

Example X

A coating containing roughly the same B, C, Ni,and W content as Coating 11, of Example I, was prepared from another powder mix, using a plasma torch instead of the detonation gun used to deposit Coating #1. The porosity in this coating ranged from 3% to 6% in different samples, making it substantially inferior to coating #1.

Example XI

Coatings were prepared by detonation gun deposition of mixtures of the WC-CO powder described in Example I with varying amounts of Ni-B alloy 1 and Ni-B alloy 2 on the two large faces of 1" x 3" x 6" blocks of AISI 4140 steel, then heat treated first at over 1000°C to treat the coating and subsequently reheated to about 850°C, quenched in oil, reheated again at a lower temperature to temper the steel to about HRC 30 and examined for cracks using fluorescent penetrant. No cracks were found in any of these coatings. The specific compositions of these coatings are listed in the following Table IV. Each of these coatings was not measurably different from Coating #1 in resistance to high stress abrasion and had no more porosity than Coating II.

TABLE IV

-----Mix Composition-----					
WC-Co	Ni-B Alloy 1	Ni-B Alloy 2	Wt % B in Ni-B Alloys	Percent Boron In Pwdr	Percent Boron In Ctng
**65.0	6.0	29.0	4.88	1.7	2.2
65.0	5.0	30.0	4.57	1.6	2.0
62.0	5.0	33.0	4.45	1.7	2.2
60.0	5.0	35.0	4.38	1.8	2.3
57.0	5.0	38.0	4.28	1.9	2.3
67.0	4.0	29.0	4.33	1.5	1.9

** This composition is designated Coating #1 in the text.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A coated article which comprises a steel body and a superimposed coating with said coating having an as-deposited porosity of less than 5% and a composition consisting essentially of a metal carbide, metal binder and fraction, said metal carbide consisting essentially of one or more carbides selected from tungsten, chromium, vanadium, hafnium, titanium, zirconium, niobium, molybdenum and tantalum carbides and compounds thereof along with a metal binder selected from Co, Ni, Fe and alloys thereof and a fraction consisting of a nickel-based boron containing alloy of such composition that boron constitutes 1.3 and 3.0 wt% of the coating, said metal carbide(s) and metal binder fraction constituting between 50 wt% and 75 wt% of the entire composition, with said metal binder being present in an amount which is a maximum of 25 wt% of the metal carbide plus binder fraction and with said nickel based boron-containing alloy representing the balance of the composition, with a boron content in said nickel based boron-containing alloy in a range of between 4 wt% and 5 wt%.

2. An article as claimed in claim 1, wherein said nickel-based boron-containing alloy comprises a first and second component with said first component containing 13 to 14 wt% boron and constituting 4 to 8 wt% of the coating composition and with said second component containing 2 to 4 wt% boron and alloying elements selected from the elements consisting of chromium, iron and silicon.

3. An article as claimed in any one of claims 1 and 2, wherein the coating upon heat treatment to above a heat treatment temperature of at least 950°C forms a nickel alloy matrix containing compounds of one or more carbide(s) and boride(s) with said heat treated coating having a hardness above 8,82 Gpa (900 Kg/mm^2) Hv.3, being metallurgically bonded to the said body, and having a porosity which is a maximum of 90% of the as-deposited coating said porosity being present only in the form of isolated enclosed pores.

4. A process for coating a steel body to form an article with a wear and corrosion resistant surface comprising the steps of: preparing a powder composition of a metal carbide, metal binder and fraction, wherein said metal carbide consists essentially of at least one metal carbide selected from tungsten, chromium, vanadium, hafnium, titanium, zirconium, niobium, molbdenum and tantalum carbides and compounds thereof, the metal binder is selected from the elements consisting of cobalt, nickel, iron and alloys thereof, and the fraction consists of a nickel based boron-containing alloy in which the metal carbide and the metal binder in the powder composition comprise between 50 and 75 wt% of the powder composition with the metal binder being present in an amount of which is a maximum of 25 wt% of the composition of said fraction and with said nickel based boron containing alloy representing the balance of the composition, with a boron content in said at least one metal-based boron-containing alloy in a range of between 4 wt% and 5 wt%, depositing said powder composition by a thermal spray process and heating the coating to a temperature above 950°C to

produce a coated with less than 5% included porosity and such that the boron content of the coating lies in the range of 1.3 wt% to 3.0 wt% of the total coating composition.

5. A process as claimed in claim 4, wherein deposition is by means of a detonation gun and the boron content of the powder is between 1.0 and 2.7 wt%.

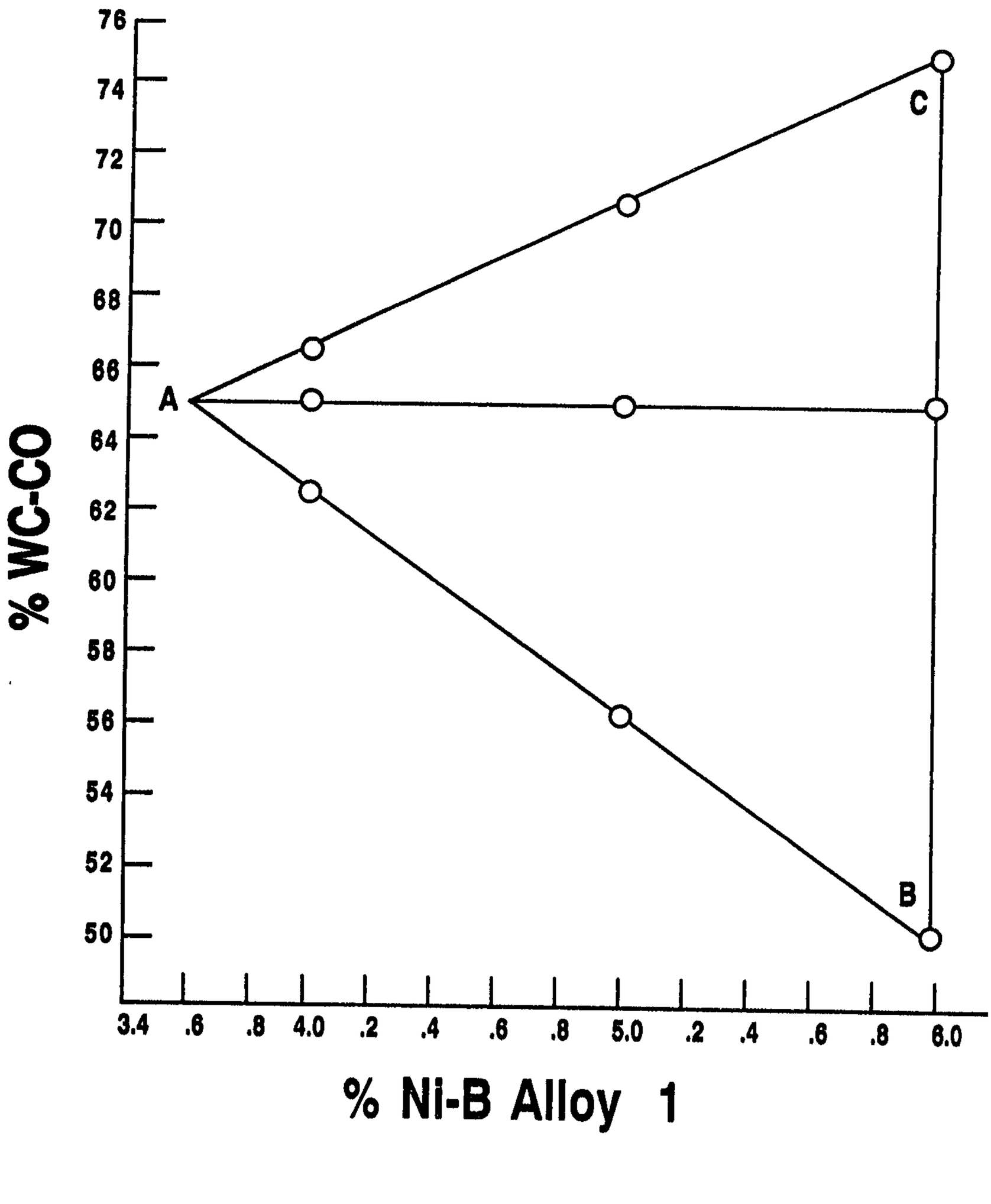
6. A process as claimed in claim 5, in which the boron content is between 1.4 and 2.2 wt%.

7. A process as claimed in claim 5, in which said metal carbide(s) comprise tungsten carbide(s) and said metal binder consists essentially of cobalt.

8. A process of claimed in claim 5, in which said metal binder constitutes between 6 and 15 wt% of the carbide and binder fraction.

9. A process as claimed in claim 8, in which said boron-containing alloy comprises a first and second component with said first component containing 13 to 14 wt% boron and constituting about 3.6 to 6 wt% of the powder and with said second component containing 2 to 4 wt% boron and also containing alloying elements selected from the elements consisting of chromium, iron and silicon.

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