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(54) Title: FUNCTIONALLY GRADED CARBIDES

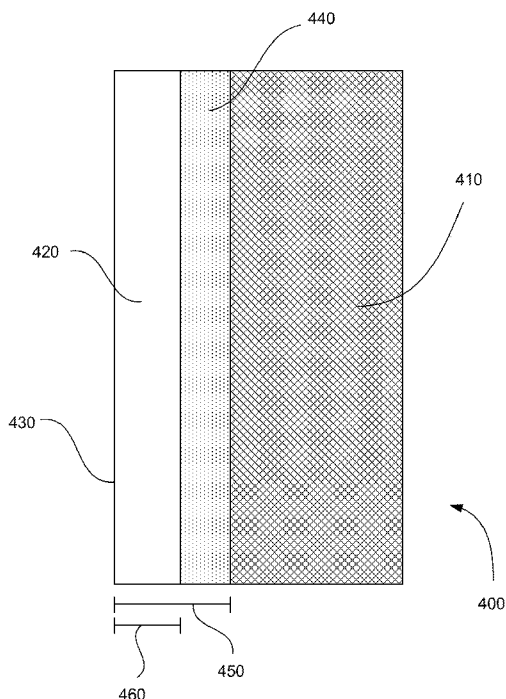


FIG. 4

(57) Abstract: A functionally graded carbide body (400) can include a group 5 metal carbide substrate having a bulk composition region (410) that contains at least 70 wt% of a rhombohedral ζ -phase carbide. A γ -phase-rich region (420) having a γ -phase-rich composition can be at a surface (430) of the substrate, and a phase composition gradient region (440) can transition from the γ -phase-rich composition region at the surface to the bulk composition region at a gradient depth (450) below the surface.



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FUNCTIONALLY GRADED CARBIDES

RELATED APPLICATION

This application claims priority to U.S. Provisional Patent Application No. 62/125,488, filed January 22, 2015 which is incorporated herein by reference.

BACKGROUND

Hard materials, used in such applications as cutting tools for machining and wear inserts in rock drilling tools, have evolved from high-speed tools steels, to cemented carbides, cermets, ceramics, polycrystalline cubic boron nitride (CBN) and polycrystalline diamond (PCD). This evolution was driven by the need for higher hardness, particularly at high temperatures, to reduce wear at higher cutting speeds to increase productivity. But, the increased hardness has been achieved at the expense of fracture toughness, and the low toughness ceramic tools have been limited to applications with low feed rates and uninterrupted cutting.

Ideally, a tool material should possess a combination of high hardness to resist wear and abrasion, high fracture toughness to resist thermal and mechanical shock, and chemical and thermal stability to resist interaction with the stock. The requirements of high hardness and high fracture toughness are not easy to achieve in a single-phase material via control of the microstructure. A fine grain size, for example, enhances hardness, usually at the expense of fracture toughness. Even in two-phase materials designed for wear and abrasion resistance, such as cemented carbides (WC + Co) and cermets (TiC + Ni), the relative amounts of the carbide phase and the binder phase are optimized to achieve a compromised combination of hardness and fracture toughness.

SUMMARY

A functionally graded carbide body of a group 5 metal carbide can have a γ -phase-rich region at one or more surfaces. The body can have a bulk composition region that includes at least 70 wt% of a rhombohedral ζ -phase carbide. A phase composition gradient region can transition from the γ -phase-rich composition region at the surface to the bulk composition region at a gradient depth below the surface.

A method of making a functionally graded carbide body can include obtaining a group 5 metal carbide substrate having a bulk composition region comprising at least 70 wt% of a rhombohedral ζ -phase carbide. A surface of the group 5 metal carbide substrate can be treated with a carbon-containing gas at a carburization temperature. This can form a γ -phase-rich region having a γ -phase-rich composition region at the surface and a phase composition gradient region transitioning from a γ -phase-rich composition region at the surface to the bulk composition region at a gradient depth below the surface.

Additional features and advantages of these principles will be apparent from the following detailed description, which illustrates, by way of example, features of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a phase diagram of the tantalum-carbon (Ta-C) binary system.

FIG. 2 shows a phase diagram of the niobium-carbon (Nb-C) binary system.

FIG. 3 shows a phase diagram of the vanadium-carbon (V-C) binary system.

FIG. 4 shows a schematic cross-sectional view of a functionally graded carbide body in accordance with an embodiment of the present technology.

FIG. 5 shows a conceptual graph of phase content and carbon to group 5 metal atomic ratio vs. depth beneath a surface of a functionally graded carbide body in accordance with an embodiment of the present technology.

FIG. 6 shows a flowchart of a method of making a functionally graded carbide body in accordance with an embodiment of the present technology.

FIG. 7 shows a microscope image of a cross section of a functionally graded carbide body in accordance with an embodiment of the present technology.

FIG. 8 shows an X-ray diffraction (XRD) pattern of a bulk substrate having 95 wt% of ζ -Ta₄C_{3-x} and 5 wt% γ -TaC_y in accordance with an embodiment of the present technology.

FIG. 9 shows an X-ray diffraction (XRD) pattern of a 100 wt% γ -TaC_y surface layer of a functionally graded carbide body in accordance with an embodiment of the present technology.

FIG. 10 is a graph of Knoop microhardness ($HK0.1$) vs. distance from the surface of a functionally graded carbide body in accordance with an embodiment of the present technology.

It should be noted that the figures are merely exemplary of several embodiments and no limitations on the scope of the present invention are intended thereby. Further, the figures are generally not drawn to scale, but are drafted for purposes of convenience and clarity in illustrating various aspects of the invention.

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DETAILED DESCRIPTION

Reference will now be made to exemplary embodiments and specific language will be used herein to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended. Alterations and further
10 modifications of the inventive features described herein, and additional applications of the principles of the invention as described herein, which would occur to one skilled in the relevant art and having possession of this disclosure, are to be considered within the scope of the invention. Further, before particular embodiments are disclosed and described, it is to be understood that this invention is not limited to the particular process
15 and materials disclosed herein as such may vary to some degree. It is also to be understood that the terminology used herein is used for the purpose of describing particular embodiments only and is not intended to be limiting, as the scope of the present invention will be defined only by the appended claims and equivalents thereof.

Definitions

20 In describing and claiming the present invention, the following terminology will be used.

The singular forms “a,” “an,” and “the” include plural references unless the context clearly dictates otherwise. Thus, for example, reference to “a surface” includes reference to one or more of such structures, “a carbide body” includes reference to one or
25 more of such materials, and “a treating step” refers to one or more of such steps.

As used herein, “substantial” when used in reference to a quantity or amount of a material, or a specific characteristic thereof, refers to an amount that is sufficient to provide an effect that the material or characteristic was intended to provide. The exact degree of deviation allowable may in some cases depend on the specific context.
30 Similarly, “substantially free of” or the like refers to the lack of an identified element or agent in a composition. Particularly, elements that are identified as being “substantially free of” are either completely absent from the composition, or are included only in amounts which are small enough so as to have no measurable effect on the composition.

As used herein, “about” refers to a degree of deviation based on experimental error typical for the particular property identified. The latitude provided the term “about” will depend on the specific context and particular property and can be readily discerned by those skilled in the art. The term “about” is not intended to either expand or limit the degree of equivalents which may otherwise be afforded a particular value. Further, unless
5 otherwise stated, the term “about” shall expressly include “exactly,” consistent with the discussion below regarding ranges and numerical data.

As used herein, “group 5 metal” refers to any metal in the fifth group of the periodic table. In many embodiments of the present technology, the group 5 metal can be
10 vanadium, niobium, or tantalum.

As used herein, “phase composition gradient” refers to a change in an amount of at least one phase present in a carbide material over a finite distance. For example, a phase composition gradient can transition from a first carbide phase to a second carbide phase. However, the phase composition gradient does not necessarily transition between
15 pure phases. A phase composition gradient generally can transition from a first composition of one or more phases to a second composition with different phase contents. In one example, a phase composition gradient transitions from a substantially pure γ -phase group 5 metal carbide to a bulk composition that includes a majority of a ζ -phase group 5 metal carbide with a small amount of the γ -phase carbide. A phase composition
20 gradient can transition gradually from first phase composition to the second phase composition. While phase composition can vary, corresponding chemical composition can remain constant or vary across the phase composition gradient, although at equilibrium chemical composition can generally be constant over a phase composition gradient region. Thus, the phase composition gradient does not have discrete boundaries
25 between different phase compositions, as would occur when a layer of one phase of carbide material is deposited onto another phase of carbide material.

As used herein, “chemical composition gradient” refers to a change in relative amounts of atomic elements in a material. For example, in a group 5 metal carbide, a chemical composition gradient can refer to a change in relative amounts of carbon and
30 group 5 metal atoms. Such a chemical composition gradient transitions from one carbon to group 5 metal atomic ratio to another ratio. In some cases, a single phase of a group 5 metal carbide can exist over a range of different chemical compositions, e.g., relative amounts of carbon and metal atoms. Therefore, a region having a single, pure carbide

phase can have a chemical composition gradient in the region as long as the carbon to metal atomic ratio remains within the stable range for the carbide phase (e.g. reference to a corresponding phase diagram).

As used herein, “pure carbide” refers to a material that contains only carbide, without a metal binder as is used in cemented carbides. The term “pure carbide” does not imply that the material has a uniform phase composition or metal/carbon ratio throughout the entire material. For example, in a pure tantalum carbide, the ratio of tantalum to carbon can vary either in a single phase, or by forming multiple different phases of tantalum carbide. Nevertheless, the entire tantalum carbide material is still referred to as a pure carbide.

As used herein, “Knoop hardness” and “ $HK0.1$ ” refer to a hardness score of a material using the Knoop microhardness test. This test is performed by pressing a diamond indenter into a surface with a known load, in this example 0.1 kg. The long diagonal of the resulting impression is measured, and the Knoop hardness, $HK0.1$, in units of GPa is calculated using the following formula given in ASTM Standard C 1326-03 Standard Test Method for Knoop Indentation Hardness of Advanced Ceramics:

$$HK0.1 = 0.014229 \left(\frac{P}{d^2} \right)$$

(1)

In Eq. (1), P is the indentation load in Newtons, and d is the long diagonal of the Knoop impression in mm.

As used herein, “fracture toughness” and “ K_{Ic} ” refer to a property describing the ability of a material containing a crack to resist fracture. Values of K_{Ic} reported herein were measured using the single-edge-precracked-beam test described in ASTM Standard C 1421-10 Standard Test Methods for Determination of Fracture Toughness of Advanced Ceramics at Ambient Temperature.

Concentrations, dimensions, amounts, and other numerical data may be presented herein in a range format. It is to be understood that such range format is used merely for convenience and brevity and should be interpreted flexibly to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a range of about 1 to about 200 should be interpreted to include not only the explicitly recited limits of 1 and

200, but also to include individual sizes such as 2, 3, 4, and sub-ranges such as 10 to 50, 20 to 100, etc.

As used herein, a plurality of items, structural elements, compositional elements, and/or materials may be presented in a common list for convenience. However, these
5 lists should be construed as though each member of the list is individually identified as a separate and unique member. Thus, no individual member of such list should be construed as a de facto equivalent of any other member of the same list solely based on their presentation in a common group without indications to the contrary.

10 *Functionally Graded Carbides*

Functional grading is an approach to tailoring microstructure and mechanical properties of a hard material for wear and abrasion applications. For example, functional grading of cemented carbides can be achieved by sintering techniques that lead to either a binder-free surface layer or a graded binder content increasing from the surface to the
15 bulk. Functionally-graded cemented carbide cutting tools have shown improved performance in metal cutting relative to conventional cutting tools. The improved performance has been attributed to both the graded microstructure that produces a hard surface and a tough interior and a compressive residual stress produced in the surface region due to gradients in density or thermal-expansion mismatch associated with
20 gradients in phase distribution.

Pure carbides are a class of materials that is entirely made up of carbides. Thus, pure carbides are distinct from cemented carbides, in which carbide particles are bound together by a metallic binder. The present disclosure describes functionally graded carbides that can be pure or substantially pure carbides. Functionally graded pure carbides
25 can provide advantages over functionally graded cemented carbides. Pure carbides typically have much higher melting temperatures than the metals used as binders in cemented carbides. This property allows functionally graded pure carbides to retain their enhanced hardness and fracture toughness properties at higher operating temperatures than cemented carbides. Additionally, pure carbides can have better corrosion resistance
30 than cemented carbides. Engineered surface coatings and laminated carbide ceramics represent some progress in the direction of functionally graded pure carbides. But, true functional grading via tailoring of microstructure or phase content has been elusive due to difficulty in tailoring the near-surface microstructure during processing or obtaining high

hardness and high fracture toughness in the same ceramic system by changing the microstructure or phase distribution.

The tantalum-carbon (Ta-C) binary system allows for functional grading because of the presence of two carbides, adjacent to each other on the phase diagram, with widely differing mechanical properties. These carbides can be seen on the phase diagram of the Ta-C binary system shown in FIG. 1. The two carbides are γ -TaC_y ($0.78 \leq y \leq 1$), a hard and brittle face-centered-cubic (fcc) carbide and a tough, but not hard, rhombohedral carbide, ζ -Ta₄C_{3-x} ($0.28 \leq x \leq 0.4$). The ζ -phase carbide can be formed in a nearly-single-phase, polycrystalline substrate having near theoretical density by reaction sintering of Ta and γ -TaC powder mixtures with or without the application of pressure. Methods for forming such bulk ζ -Ta₄C_{3-x} carbides are described in WO/2010/008839, U.S. Patent No. 8,685,874, and U.S. Patent Application No. 14/742,616, which are each hereby incorporated by reference.

Each phase of tantalum carbide has unique properties. The γ -TaC_y phase has a high hardness ($H = 13.5$ - 20 GPa) but lower fracture toughness ($K_{Ic} = 3.8$ - 5.3 MPa $\sqrt{m}$). The ζ -Ta₄C_{3-x} phase has a high fracture toughness ($K_{Ic} = 13.5$ - 15.5 MPa $\sqrt{m}$) but a lower hardness ($H = 5.5$ - 7 GPa). There is also an α -Ta₂C_y phase at C/Ta ratios from 0.44 to 0.5. This phase has intermediate hardness and fracture toughness ($H = 9.3$ GPa and $K_{Ic} = 8.3$ MPa $\sqrt{m}$). Thus, ζ -Ta₄C_{3-x} exhibits high fracture toughness. The ζ -Ta₄C_{3-x} phase also exhibits rising-crack-growth-resistance (R-curve) behavior that is associated with bridging of cracks by lamellae formed by the easy cleavage of basal planes of the ζ -phase.

Similar carbide phases exist for the other group 5 metals, niobium and vanadium. FIG. 2 shows a phase diagram for the niobium-carbon (Nb-C) binary system. The Nb-C system has a ζ -Nb₄C_{3-x} phase next to a γ -NbC_y phase. FIG. 3 shows a phase diagram for the vanadium-carbon (V-C) binary system. The V-C system also has a ζ -V₄C_{3-x} phase next to a γ -VC_y phase. These phases allow functionally graded carbides to be formed using niobium carbide and vanadium carbide. Although much of the description herein focuses on tantalum carbides, the functionally graded carbides and methods of making functionally graded carbides disclosed herein can also include niobium carbides and vanadium carbides.

With this description in mind, the present technology encompasses functionally graded carbides. In one embodiment, a functionally graded carbide body can include a group 5 metal carbide substrate. The substrate can have a bulk composition comprising at

least 70 wt% of a rhombohedral ζ -phase carbide. The functionally graded carbide body can also include a γ -phase-rich region having a γ -phase-rich composition region at a surface of the group 5 metal carbide substrate. A phase composition gradient region can transition from the γ -phase-rich composition region at the surface to the bulk composition region at a gradient depth below the surface. Although the functionally graded carbide body can typically be a pure carbide, the body can optionally include additives such as, but not limited to, binders, alloying elements, interstitial additives, and the like.

FIG. 4 shows a schematic cross-sectional view of a functionally graded carbide body according to an example of the present technology. A group 5 metal substrate 400 has a bulk composition region 410. The bulk composition is at least 70 wt% of the rhombohedral ζ -phase carbide. A γ -phase-rich region 420 having a γ -phase-rich composition region is at the surface 430 of the substrate. A phase composition gradient region 440 transitions from the γ -phase-rich composition region to the bulk composition region 410 at a gradient depth 450 below the surface 430. Specifically, the gradient depth 450 is the depth below the surface 430 at which the phase composition gradient reaches the same composition as the bulk composition region 410. The particular embodiment shown in the figure also has a first depth 460 at which the γ -phase-rich region 420 ends and the phase composition gradient region 440 begins to transition to the bulk composition region 410. In this region, the amount of γ -phase present decreases while the amount of ζ -phase increases, until the bulk composition is reached at the gradient depth 450.

In order to clarify the phase composition gradient described above, FIG. 5 shows a conceptual graph of phase content and carbon to group 5 metal atomic ratio vs. depth beneath a surface of a functionally graded carbide body in accordance with an embodiment of the present technology. The graph shows the phase content and carbon to metal ratios in the γ -phase-rich region 420, phase composition gradient region 440, and bulk composition region 410. It should be noted that FIG. 5 is not drawn to scale and is intended only to represent these properties conceptually. As shown in FIG. 5, the γ -phase-rich region has a phase content of 100% γ -phase. However, the carbon content in this region is not uniform (e.g. exhibits a chemical composition gradient). The carbon to metal atomic ratio starts at 1.0 at the surface and decreases to a lower ratio at the phase composition gradient region (e.g. about 78% in the case of Ta-C). Across the phase composition gradient region 440, the carbon to metal ratio in the γ -phase is constant. This

ratio represents the lower limit of the carbon to metal ratio in the γ -phase. In the phase composition gradient region 440, the ζ -phase content increases from 0% to the bulk ζ -phase content, and the γ -phase content decreases from 100% to the bulk γ -phase content. The ζ -phase also has a constant carbon to metal ratio across the phase composition gradient region 440, and then this ratio is maintained within the bulk composition region 410. Thus, although the phase composition and chemical composition are somewhat related, these are distinct properties of the material which can vary from one another.

The present technology also encompasses methods of making functionally graded carbides. FIG. 6 shows one example of a method 500 for making a functionally graded carbide body. The method includes obtaining a group 5 metal carbide substrate having a bulk composition region comprising at least 70 wt% of a rhombohedral ζ -phase carbide 510; and treating a surface of the group 5 metal carbide substrate with a carbon-containing gas at a carburization temperature to form a γ -phase-rich region having a γ -phase-rich composition region and a phase composition gradient region transitioning from the γ -phase-rich composition region at the surface to the bulk composition region at a gradient depth below the surface 520. Various aspects of these and other embodiments of functionally graded carbides and methods of making functionally graded carbides are described in more detail below.

The functionally graded carbide body shown in FIG. 4 has a simple shape with a single flat surface that has been modified to form a phase composition gradient. However, functionally graded carbide bodies can be made having any desired shape, including planar and contoured surfaces. The functionally graded carbide bodies can be useful as cutting tools, drill bits, wear inserts, balls and seats in ceramic valves, high-pressure and high-temperature anvils used in diamond synthesis, or any other tool or object requiring high hardness, fracture toughness, temperature resistance, and/or corrosion resistance. The phase composition gradient is formed by exposing surfaces of a carbide substrate to a carbon-containing gas. Therefore, the substrate can have any desired shape, even complex shapes such as in drill bits, and all exposed surfaces can be treated with the carbon containing gas to form the phase composition gradient.

Because this process forms the γ -phase-rich region and phase composition gradient region by transforming a portion of the ζ -phase carbide to γ -phase carbide, as opposed to adding a layer of additional γ -phase material onto the ζ -phase substrate, the process does not substantially change the size or shape of the substrate. Therefore, the

substrate can be formed to have the final desired size and shape of the final functionally graded carbide body before the carburization treatment is performed. The carburization treatment does not substantially change the dimensions of the substrate, so the final functionally graded carbide body will retain the same dimensions. In some examples, the substrate can be formed by sintering a particulate mixture in the desired shape of the final functionally graded carbide body. In other embodiments, the substrate can be milled or otherwise machined to the desired shape before the carburization treatment. Because the ζ -phase is softer than the γ -phase, the soft ζ -phase can advantageously be milled to the desired final shape, and then a hard γ -phase surface can be formed through the carburization treatment described herein. After the carburization treatment, no additional milling is necessary because the dimensions of the substrate do not change during the treatment.

The substrate can be formed of a group 5 metal carbide. For example, the substrate can be tantalum carbide, niobium carbide, vanadium carbide, or combinations thereof. In some embodiments, the substrate can be a pure or substantially pure carbide. In other words, the substrate can be entirely or substantially made up of only a group 5 metal carbide, without a metallic binder as is used in cemented carbides.

In additional embodiments, the group 5 metal carbide substrate can have a bulk composition region comprising at least 70 wt% of the rhombohedral ζ -phase. In other embodiments, the bulk composition region can include more of the ζ -phase, such as at least 80 wt%, at least 90 wt%, or at least 95 wt% of the ζ -phase. Using certain methods of forming the group 5 metal substrate, even higher amounts of the ζ -phase can be obtained in the substrates. Other components of the bulk composition region can include γ -TaC_y and/or α -Ta₂C_y. In some examples, the bulk composition region can include less than 20 wt%, less than 15 wt%, less than 10 wt%, or even less than 5 wt% of the γ -TaC_y phase. In further examples, the bulk composition region can include less than 10 wt%, less than 5 wt%, or less than 2 wt% of the α -Ta₂C_y phase.

In certain embodiments, the overall carbon to group 5 metal atomic ratio of the bulk composition region can be in the range that theoretically allows for a pure ζ -phase. In the case of tantalum carbide, the bulk composition region can have a carbon to tantalum atomic ratio from about 0.65 to about 0.68. In the case of niobium carbide, the bulk composition region can have a carbon to niobium atomic ratio of about 0.67 to about 0.68. In the case of vanadium carbide, the bulk composition region can have a carbon to

vanadium atomic ratio of about 0.61 to about 0.62. In other embodiments, the carbon to group 5 metal atomic ratio can be outside these ranges while still being sufficient to produce a bulk composition region that is at least 70 wt% of the ζ -phase.

5 The group 5 metal carbide substrate can be obtained by mixing powders containing the group 5 metal and carbon, and then sintering the powders to form the substrate. In one embodiment, the group 5 metal carbide substrate can be obtained by assembling a particulate mixture of a group 5 metal source powder and a carbon source powder. The particulate mixture can then be sintered to form the group 5 metal carbide substrate having a bulk composition region comprising at least 70 wt% of the
10 rhombohedral ζ -phase.

In certain examples, the group 5 metal source powder can be a pure group 5 metal powder or a group 5 metal hydride powder. In one example, the group 5 metal source powder can be tantalum hydride powder. Tantalum hydride can exist in multiple phases. For example, the tantalum hydride powder can include α -, β -, γ -, δ -, ϵ -, or ζ -phase
15 tantalum hydride. In some cases, the tantalum hydride powder used in the present technology can include β -phase TaH_x . In some cases, the tantalum hydride powder can be prepared by hydrogenation of a tantalum metal powder. This can be performed as a step in the method of forming the ζ -phase tantalum carbide. Alternatively, a commercially available tantalum hydride powder can be obtained and used in the process. The group 5
20 metal source powder can have an average particle size of 2-20 μm , or in some cases 5-10 μm . Further, the group 5 metal source powder can have a bimodal size distribution, with small single particles and larger agglomerations of particles. For example, tantalum hydride powder can have a primary distribution of single particles with an average particle size of 2-5 μm and a secondary distribution of agglomerates with an average
25 agglomerate size of 5-20 μm . Smaller and more uniform particle sizes can be useful for obtaining both high green density and high sintered density. In further examples, metallic tantalum powder can be used as the group 5 metal source powder.

The carbon source powder can include graphite powder, amorphous carbon powder, group 5 metal carbide powder, or combinations thereof. In one example, γ -phase
30 tantalum carbide can be used as the carbon source powder. In further examples, any tantalum carbide powder with the formula TaC_y can be used where y is greater than about 0.68. Use of γ -TaC powder as the carbon source instead of carbon powder can provide better control of chemistry by limiting carbon volatilization during pressureless sintering.

The carbon source powder can have an average particle size from about 0.5 μm to about 20 μm . In some examples, γ -TaC powder can have an average particle size that is roughly the same as the tantalum hydride powder described above. In other examples, the γ -TaC powder can have an average particle size that is less than the tantalum hydride powder. In one example, the γ -TaC powder can have an average particle size of less than about 2 μm and often less than about 1 μm .

The group 5 metal source powder and carbon source powder can be mixed in an appropriate ratio to provide a carbon to group 5 metal atomic ratio within or near the ζ -phase range. The particulate mixture can then be formed into a compact and sintered. In some embodiments, the sintering process can be performed at low pressure, such as from about 0.01 atm to about 2 atm. In other embodiments the sintering can be performed by hot-pressing or hot-isostatic-pressing. The sintering temperature can be from about 1350 $^{\circ}\text{C}$ to about 1900 $^{\circ}\text{C}$. In other examples, the sintering temperature can be from about 1700 $^{\circ}\text{C}$ to about 1900 $^{\circ}\text{C}$. The sintering can be performed for a hold time from about 600 s to about 60,000 s. In a particular example, the sintering can be performed for a hold time from 600 s to 6,000 s. In another particular example, the sintering can be performed for a hold time sufficient to reach a densification of at least 90% and in some cases at least 94%. The compact can often be pressureless sintered to greater than 94% of theoretical density. In a further example, the compact can be pressureless sintered to greater than 97% of theoretical density. The final sintered material can include a majority of ζ -phase with smaller amounts of γ -phase and trace amounts of group 5 metal oxides. If high pressure sintering methods are used, the compact can optionally be sintered to even higher densities, such as greater than 99% of the theoretical density. High pressure sintering methods can also in some cases result in a higher ζ -phase content. However, pressureless sintering can be used to obtain sintered materials with more than 80 wt%, more than 85 wt%, or more than 86 wt% of the ζ -phase.

After the group 5 metal carbide substrate is obtained, a surface of the substrate can be treated with a carbon-containing gas to form a γ -phase-rich region and phase composition gradient region at the surface. The carbon-containing gas can include a hydrocarbon such as methane, ethane, propane, butane, natural gas, mixtures thereof, or the like as a carbon source. During the treatment, the carbon containing gas can provide carbon atoms that are adsorbed on the surface and diffuse into the substrate. The additional carbon atoms convert a portion of the substrate near the surface from the ζ -

phase to the γ -phase. This forms a γ -phase-rich transformed layer at the surface. Because the amount of carbon diffused into the substrate decreases continuously with increasing depth beneath the surface, an overall chemical composition gradient can form that transitions continuously from a 1:1 carbon to group 5 metal atomic ratio at the surface to a ratio corresponding to the ζ -phase at a gradient depth below the surface. This results in a γ -phase-rich region at the surface, which transitions to the bulk phase composition through a phase composition gradient. As used herein, "gradient depth" refers to the depth at which the composition reaches the bulk composition region of the substrate, or in other words, the depth at which the phase composition gradient ends. Accordingly, during treatment, the gradient depth and γ -phase-rich depth progressively increase from zero to a desired gradient depth as carbon diffuses into the substrate.

In some embodiments, the carbon-containing gas can be a mixture of a carbon source gas, such as a hydrocarbon, and one or more other gases. The gases in the mixture can be non-oxidizing gases. In some cases the gas mixture can include a reducing gas. In certain embodiments, the carbon-containing gas can include a mixture of a hydrocarbon and hydrogen. In one particular embodiment, the carbon-containing gas can be a mixture of methane and hydrogen. In further embodiments, the methane or other hydrocarbon can be present at a concentration of about 1 wt% to 10 wt% in the carbon-containing gas. In one particular embodiment, the carbon-containing gas can be a mixture of about 5 wt% methane in hydrogen. In still further embodiments, the carbon-containing gas can be constantly flowing so that the composition of the carbon-containing gas remains substantially constant during the carburization treatment.

The carburization treatment with the carbon-containing gas can be performed at a carburization temperature from 1200 °C to 1600 °C, and in some cases about 1270 °C to about 1500 °C. The group 5 metal carbide body can be held at a temperature in this range under the carbon-containing gas atmosphere for a sufficient time to form the phase composition gradient. In some embodiments, the treatment can be performed for a carburization time from about 10 hours to about 50 hours. Concentration of carbon in the carbon-containing gas can also affect rate of deposition, depth, and surface morphology.

On the carburized surface, the transformed phase is typically 100 wt% γ -TaC with a carbon to tantalum atomic ratio of 1. At depths below the surface, the wt% of the γ -phase can remain at 100%, while the stoichiometry, i.e., C/Ta atomic ratio decreases from 1 to about 0.78 at a transition depth indicated by the maximum hardness. Below this

depth, weight percent of the γ -phase decreases and the weight percent of the ζ -phase increases until the bulk substrate composition is reached. Within the bulk composition region, the carbon to metal ratio can once again vary, and in the case of TaC can often vary from about 0.68 to a bulk value of 0.66.

5 Group 5 metal carbides can exist in the γ -phase over a range of carbon to group 5 metal atomic ratios. For example, if the group 5 metal is tantalum, then the γ -phase can exist at carbon/tantalum atomic ratios from about 0.78 to 1.0. Above a ratio of 1.0, which is the stoichiometric ratio for γ -phase TaC_y, a mixture of γ -phase TaC_y and pure carbon will be present. Most often the C/Ta atomic ratio can be 1.0 at the outer surface of the γ -phase-rich region. In another example, if the group 5 metal is niobium, then the γ -phase
10 can exist at carbon/niobium atomic ratios from about 0.73 to 1.0. In a further example, if the group 5 metal is vanadium, then the γ -phase can exist at carbon/vanadium atomic ratios from about 0.70 to about 0.88. Therefore, in various embodiments, the γ -phase-rich composition region can have a carbon to group 5 metal atomic ratio within one of these
15 ranges. In some cases, a layer of pure carbon can be formed on the surface, and the layer of pure carbon can be in equilibrium with pure γ -phase at the surface. Generally, the γ -phase-rich region can have 70% or greater γ -phase composition, and often greater than about 90% γ -phase.

 The γ -phase-rich region can begin at the surface with the γ -phase-rich
20 composition and the phase composition gradient region can transition slowly from the γ -phase-rich composition to the bulk composition that is made up of mostly ζ -phase. In some cases, the γ -phase-rich composition can have a carbon to group 5 metal atomic ratio that decreases with increasing depth below the surface. In one example, the carbon to group 5 metal atomic ratio can be at or about 1.0 at the surface, and then the ratio can
25 continuously decrease with increasing depth. Because the γ -phase can exist at the range of carbon to group 5 metal atomic ratios, this results in a layer of γ -phase carbide with substantially no ζ -phase carbide. The ζ -phase begins to form only when the carbon to group 5 metal atomic ratio decreases below the lower limit of the γ -phase. As shown in
FIG. 4, a γ -phase-rich region 420 can extend from the surface 430 down to a first depth
30 460, at which depth the γ -phase-rich composition begins to transition to the bulk composition through a phase composition gradient region 440. In other words, substantially no ζ -phase is present between the first depth 460 and the surface. In this range, a layer of substantially pure γ -phase can be formed, although the carbon to group 5

metal atomic ratio can vary within this layer. In the phase composition gradient region, the carbon to metal ratio in the γ -phase remains constant at the lower limit of the ratio for the γ -phase, while the carbon to metal ratio in the corresponding ζ -phase also remains constant as illustrated in FIG. 5. However, the overall carbon to metal ratio of the material
5 continues to decrease through the phase composition gradient region as more and more of the ζ -phase forms, until the bulk composition region 410 is reached at the gradient depth 450.

Thus, in some embodiments, a functionally graded carbide body can have a layer of pure or substantially pure γ -phase down to a first depth, at which depth the ζ -phase is
10 present. The region where the ζ -phase content increases while the γ -phase content decreases is referred to as the phase composition gradient region. The amount of ζ -phase can increase until the gradient depth, at which depth the phase composition reaches the bulk composition. In some cases, this phase composition gradient can be continuous. As used herein, “continuous” does not necessarily imply that the rate of change of relative
15 amounts of γ -phase and ζ -phase is uniform over the entire region, or that the relative amounts of the γ -phase and ζ -phase are necessarily changing at every point in the gradient. Rather, the gradient is “continuous” because it is not discontinuous. In other words, the gradient does not include any discontinuities, such as a sharp boundary between γ -phase and ζ -phase. Such sharp boundaries can form in other processes such as
20 deposition processes, in which a layer of one phase is deposited onto a surface of another phase. In contrast, the carburization process described herein does not add a layer of new material. Instead, the process transforms the substrate material at a surface by adding carbon atoms that diffuse into the surface. The concentration of diffused carbon atoms naturally decreases with increasing depth below the surface, forming a gradient.

25 The gradient depth can be controlled by the carburization temperature, carburization time, and concentration of the carbon-containing gas. In some embodiments, the gradient depth can be from about 5 micrometers to about 50 micrometers. In further embodiments, the gradient depth can be from about 10 micrometers to about 25 micrometers. The depth at which the ζ -phase begins to appear
30 can also vary depending on carburization temperature, carburization time, and concentration of the carbon-containing gas. In some embodiments, this first depth can be from about 2 micrometers to about 30 micrometers. In further examples, this first depth can be from about 5 micrometers to about 10 micrometers.

In certain examples, the γ -phase-rich composition can have a carbon to group 5 metal atomic ratio of about 1.0 at the surface (or, in the case of vanadium, about 0.88). The ratio can decrease with increasing depth below the surface down to the lower limit of the ratio for the γ -phase. At this point, ζ -phase carbide can appear and the relative amount of ζ -phase can increase until the bulk composition is reached at the gradient depth.

It has been found, however, that forming a γ -phase-rich composition with a carbon to group 5 metal atomic ratio of 1.0 at the surface may not provide the maximum surface hardness for the functionally graded carbide. Without being bound to a specific theory, it is believed that reducing the carbon to group 5 metal atomic ratio below the stoichiometric ratio of 1.0 can increase the hardness of the γ -phase carbide. Thus, a γ -phase carbide having a lower ratio can actually be harder than a stoichiometric γ -phase with a ratio of 1.0. Experiments have shown that the hardness increases as the ratio decreases all the way to the lower limit ratio, where ζ -phase carbide begins to appear. Therefore, the surface hardness of the functionally graded carbide body can be increased by forming the chemical composition gradient such that the γ -phase-rich composition at the surface has a carbon to group 5 metal atomic ratio of less than 1.0. In certain embodiments, the γ -phase-rich composition can have a carbon to group 5 metal atomic ratio of about 0.78 to about 0.85 at the surface. In a particular embodiment, the γ -phase-rich composition can have a carbon to group 5 metal atomic ratio of about 0.8. This can provide a greater surface hardness for the functionally graded carbide body.

The carburization treatment tends to naturally form a chemical composition gradient that starts with the stoichiometric ratio of carbon to group 5 metal at the surface. Thus, in some embodiments, the carburization treatment can produce a functionally graded carbide body with a carbon to group 5 metal ratio of about 1.0 at the surface. In order to obtain a lower ratio at the surface, the functionally graded carbide body can be annealed to partially decarburize the surface. The annealing treatment can be performed at an annealing temperature in a de-carburizing atmosphere, such as hydrogen without a carbon-containing gas. Other de-carburizing atmospheres can also be used. The annealing temperature can be lower than the carburization temperature to suppress potential reverse transformation and reduction in thickness of the transformed γ -phase-rich layer. In one embodiment, the annealing temperature can be from about 1000 °C to about 1200 °C. In further embodiments, the annealing can be performed for a time from about 1 hour to about 10 hours. In some cases, the annealing time and temperature can be sufficient to

produce a carbon to group 5 metal atomic ratio of about 0.8 at the surface. In still further embodiments, the annealing can be performed under a hydrogen atmosphere.

In some embodiments, the annealing treatment can result in a substantially constant carbon to group 5 metal atomic ratio to a first depth from the surface within the γ -phase-rich region, and then the ratio transitions continuously to the ratio in the bulk composition at the gradient depth. In one example, the carbon to group 5 metal atomic ratio can be substantially uniform from the surface down the first depth, at which point the ratio decreases to allow the ζ -phase to form. In another example, the carbon to group 5 metal atomic ratio can be about 0.8 throughout the layer of γ -phase-rich composition down to the first depth.

By treating a group 5 metal carbide substrate having a high ζ -phase bulk composition with the carburization treatment and optionally the annealing treatment described above, a functionally graded carbide body having both high surface hardness and high fracture toughness can be formed. In some embodiments, the functionally graded carbide body can have a surface hardness $HK_{0.1}$ from about 10 GPa to about 25 GPa. In further embodiments, the functionally graded carbide body can have a fracture toughness from about 10 $\text{MPa}\sqrt{\text{m}}$ to about 15 $\text{MPa}\sqrt{\text{m}}$.

The functionally graded carbide body can also have a high fracture strength. In some cases, the γ -phase-rich composition at the surface of the carbide body can have residual compressive stress due to a mismatch in density between the γ -phase and the ζ -phase. For example, the theoretical density of γ -phase tantalum carbide is 14.47 g/cm^3 , whereas the theoretical density of ζ -phase tantalum carbide is 14.82 g/cm^3 . Therefore, when the γ -phase layer is formed during carburization, the γ -phase is dense and subjected to residual compressive stress. This compressive stress can discourage propagation of fractures, increasing the fracture strength of the functionally graded carbide body. The strength-controlling flaw size can be limited to the thickness of the γ -phase layer, and the fracture toughness of the carbide body can be the higher fracture toughness of the bulk substrate. Mismatch in coefficient of thermal expansion between the γ -phase and ζ -phase may also affect the residual stress at various temperatures.

The fracture strength of the functionally grade carbide body can also be increased by reducing the grain size of the γ -phase at the surface. In one example, this can be accomplished by carburizing the carbide substrate at a lower temperature. Carburization temperatures in the range of 1270 °C to 1500 °C can result in small grains, increasing the

fracture strength. In some embodiments, the γ -phase at the surface can have an average grain size of 1 μm to 5 μm .

Examples

Tantalum carbide monoliths were formed of $\zeta\text{-Ta}_4\text{C}_{3-x}$ in the form of type B bend
 5 bars, 4 x 3 x 45 mm in dimensions, as specified in ASTM Standard C-1161-02 for
 measurements of flexural strengths of advanced ceramics. The $\zeta\text{-Ta}_4\text{C}_{3-x}$ monoliths were
 processed by hot-pressing and contained 95 wt% of $\zeta\text{-Ta}_4\text{C}_{3-x}$. The bar specimens were
 supported on one end and the long faces were exposed to a flowing gas mixture of
 hydrogen and 5% methane (CH_4) in a tube furnace at a fixed temperature in the range of
 10 1270-1500°C for a fixed time period in the range of 10-20 hours to carburize the
 specimens.

The carburized specimens were characterized by three techniques. (a) The
 microstructure on an etched cross-section in the vicinity of the carburized surface was
 assessed using an optical microscope (Model: MEF4M, Leica, Wein, Austria). (b) Crystal
 15 phases were identified and weight percent of phases in the substrate and the carburized
 surface were estimated using an X-ray diffractometer (XRD, Model Philips X'Pert-MPD,
 PANalytical Inc., Westborough, MA) and associated software. (c) Hardness as a function
 of distance from the carburized surface on a cross section was measured using a Knoop
 microhardness tester (Model: Tukon 1202, Wilson, Shanghai, China) at 1 N load.

20 FIG. 7 shows the microstructure on the cross section in the vicinity of the outer
 surface of a $\zeta\text{-Ta}_4\text{C}_{3-x}$ specimen carburized at 1500°C for 20 hours. The four layers
 visible in FIG. 7, in sequence from left to right, are (a) the mounting material, (b) an
 electroless Ni layer used to minimize damage to the specimen edge, (c) $\gamma\text{-TaC}_y$ layer, and
 (d) $\zeta\text{-Ta}_4\text{C}_{3-x}$ substrate. The $\gamma\text{-TaC}_y$ surface layer was more resistant to etching than the $\zeta\text{-}$
 25 $\text{Ta}_4\text{C}_{3-x}$ substrate, and the transition between the two phases occurred over a short
 distance. The thickness of the transformed $\gamma\text{-TaC}_y$ layer in FIG. 7 is about 35 μm . The
 grains in the $\zeta\text{-Ta}_4\text{C}_{3-x}$ substrate were elongated and tabular with lengths in the range of
 10-20 μm and widths in the range of 5-10 μm . The grains in the $\gamma\text{-TaC}_y$ layer were not
 adequately resolved for size measurements. The thickness of the transformed surface
 30 layers carburized at 1270°C and 1470°C for 20 hours were 5 μm and 25 μm , respectively.

The XRD patterns of the bulk and of the surface layer are shown in FIG. 8 and
 FIG. 9, respectively. These figures show intensity (in arbitrary units) vs. 2θ . The small

boxes below the intensity graph represent peaks that correspond to the γ -TaC_y or ζ -Ta₄C_{3-x} phases. The diffraction pattern for the bulk was taken on a ground and polished wide surface of the bar specimen prior to carburization. The diffraction pattern for the surface was taken on the same surface after carburization and light polishing to remove the loosely adhering carbon layer. The bulk contained 95 wt% of ζ -Ta₄C_{3-x} and 5 wt% γ -TaC_y. The surface of the transformed layer was essentially 100 wt% γ -TaC_y. The lattice parameter calculated from the diffraction pattern of FIG. 9 was 4.455 Å. This corresponds to a stoichiometric composition of γ -TaC on the carburized surface based on the calibration of lattice parameter and C/Ta atomic ratio for the fcc γ -TaC_y phase.

FIG. 10 shows the variation of Knoop microhardness, $HK\ 0.1$, as a function of distance from the carburized surface. The hardness was 11.4 GPa at a distance, $x = 5\ \mu\text{m}$, from the carburized surface. The hardness increased with increasing distance from the carburized surface and reached a maximum value of 22.7 GPa at a distance of $x = 25\ \mu\text{m}$. For $x > 25\ \mu\text{m}$, the hardness decreased gradually and reached a plateau value of 9.5 GPa corresponding to the bulk ζ -Ta₄C_{3-x} phase. The drop in hardness for $x < 25\ \mu\text{m}$ was initially unexpected. However, it is believed that the maximum in hardness at $x = 25\ \mu\text{m}$ was due to non-stoichiometry in the γ -TaC_y layer.

The solid line in FIG. 10 is the following empirical sigmoidal function fitted to the data covering the range, $x = 25\ \mu\text{m}$ to $x = 55\ \mu\text{m}$:

$$H(x) = (H_\gamma - H_\zeta) \left[1 - \frac{1}{1 + e^{-\left(\frac{x-\xi}{\lambda}\right)}} \right] + H_\zeta \quad (2)$$

In Eq. (2), H_γ , H_ζ , ξ , and λ are fitting parameters with the following interpretations. H_γ is an upper-bound hardness of the γ -TaC_y layer, H_ζ is the lower-bound hardness of the ζ -Ta₄C_{3-x} bulk, ξ is a measure of the thickness of the transformed layer and corresponds to $H(\xi) = (H_\gamma + H_\zeta)/2$, and λ is a scaling parameter that defines the ‘sharpness’ of the hardness transition from the surface layer to the bulk. The solid line shown in FIG. 10 represents a ‘best fit’ of Eq. (2) resulting in the following values of the parameters: $H_\gamma = 22.4\ \text{GPa}$, $H_\zeta = 9.5\ \text{GPa}$, $\xi = 34.6\ \mu\text{m}$, and $\lambda = 2.8\ \mu\text{m}$.

The results of the experiments demonstrate the feasibility of designing and processing a functionally-graded carbide in the Ta-C system. A hard surface layer of γ -

TaC_y was formed in the surface of a soft and tough substrate of ζ -Ta₄C_{3-x} by surface carburization. The highest Knoop hardness in the γ -TaC_y layer, $HK0.1 = 22.4$ GPa, was measured at a depth of $x = 25$ μ m, while the Knoop hardness of the ζ -Ta₄C_{3-x} bulk was 9.5 GPa. The fracture toughness measured by the single-edge-precracked-beam tests were

5 5.3 MPa $\sqrt{m}$ for the stoichiometric γ -TaC phase and 13.8 MPa $\sqrt{m}$ for a composite of 95 wt% ζ -Ta₄C_{3-x} phase and 5 wt% γ -TaC_y phase. Thus, the goals of a high hardness on the surface and a high fracture toughness in the bulk were achieved by functional grading in the Ta-C system.

The variation of the Knoop microhardness within the γ -TaC_y layer, from $HK0.1 = 11.4$ GPa at $x = 5$ μ m to $HK0.1 = 22.7$ GPa at $x = 25$ μ m, was unexpected. This result

10 may be due to the following reason. At the end of the carburization treatment, the specimen was cooled rapidly from the carburization temperature, 1500°C, by switching off the tube furnace. This rapid cooling may have ‘frozen in’ a gradient in carbon concentration or the C/Ta atomic ratio in the γ -TaC_y phase from the stoichiometric value,

15 $y = 1$ at $x = 0$ to about $y = 0.8$ at a depth where both γ -TaC_y and ζ -Ta₄C_{3-x} phases co-exist. Both experiments and theoretical calculations indicate that hardness of the γ -TaC_y phase increases with decreasing value of y in the range, $y = 1$ to 0.8. For example, an increase in Vickers hardness, $HV1$, from 13.5 GPa to 20 GPa as y decreases from 1 to 0.8 has been reported. Lattice parameter measured on the carburized surface suggests a stoichiometric

20 γ -TaC phase on the surface. This is consistent with the Ta-C phase diagram since γ -TaC is in equilibrium with free carbon on the surface. The phase diagram also indicates that, $y \sim 0.8$, at 1500°C in the two-phase region consisting of γ -TaC_{0.8} and ζ -Ta₄C_{2.72}.

The above discussion of the possible role gradient in non-stoichiometry plays in causing the hardness variation within the γ -TaC_y layer suggests some avenues for

25 optimizing the chemistry of the layer for both uniform and increased hardness. Thus, for example, the stoichiometry or C/Ta ratio within the γ -TaC_y layer can be made more uniform by a homogenization or annealing treatment. This can be done by annealing the carburized specimen in a pure H₂ environment at a temperature lower than that used for carburization. The H₂ environment can promote decarburization and lower the C/Ta ratio

30 at the surface, while the lower temperature will suppress potential reverse transformation and a reduction in the thickness of the transformed layer.

It is to be understood that the above-referenced arrangements are illustrative of the application for the principles of the present invention. Thus, while the present invention has been described above in connection with the exemplary embodiments, it will be apparent to those of ordinary skill in the art that numerous modifications and alternative
5 arrangements can be made without departing from the principles and concepts of the invention as set forth in the claims.

CLAIMS

What is claimed is:

1. A functionally graded carbide body of a group 5 metal carbide, comprising:
 - 5 a bulk composition region comprising at least 70 wt% of a rhombohedral ζ -phase carbide of the group 5 metal carbide;
 - a γ -phase-rich region having a γ -phase-rich composition at a surface of the carbide body; and
 - a phase composition gradient region transitioning from the γ -phase-rich
 - 10 composition region to the bulk composition region at a gradient depth below the surface.
2. The functionally graded carbide body of claim 1, wherein the γ -phase-rich composition region is from 70 wt% to 100 wt% γ -phase.
- 15 3. The functionally graded carbide body of claim 1, wherein the phase composition gradient region transitions substantially continuously from the γ -phase-rich composition region to the bulk composition region.
4. The functionally graded carbide body of claim 1, wherein the γ -phase-rich composition
- 20 region has a substantially uniform carbon to group 5 metal atomic ratio to a first depth from the surface, and then transitions continuously to the bulk composition region at the gradient depth.
5. The functionally graded carbide body of claim 4, wherein the first depth is from 2
- 25 micrometers to 30 micrometers.
6. The functionally graded carbide body of claim 1, wherein the gradient depth is from 5 micrometers to 50 micrometers.
- 30 7. The functionally graded carbide body of claim 1, wherein the carbide body is a substantially pure carbide.

8. The functionally graded carbide body of claim 1, wherein the carbide body has a surface hardness $HK0.1$ of about 10 GPa to about 25 GPa.
9. The functionally graded carbide body of claim 1, wherein the carbide body has a bulk fracture toughness of about 10 $\text{MPa}\sqrt{\text{m}}$ to about 15 $\text{MPa}\sqrt{\text{m}}$.
10. The functionally graded carbide body of claim 1, wherein the carbide body has a residual compressive stress at the surface.
11. The functionally graded carbide body of claim 1, wherein the group 5 metal is tantalum.
12. The functionally graded carbide body of claim 11, wherein the γ -phase-rich composition region has a carbon to tantalum atomic ratio from about 0.78 to about 1.0.
13. The functionally graded carbide body of claim 1, wherein the group 5 metal is niobium.
14. The functionally graded carbide body of claim 13, wherein the γ -phase-rich composition region has a carbon to niobium atomic ratio from about 0.73 to about 1.0.
15. The functionally graded carbide body of claim 1, wherein the group 5 metal is vanadium.
16. The functionally graded carbide body of claim 15, wherein the γ -phase-rich composition region has a carbon to vanadium atomic ratio from about 0.7 to about 0.88.
17. A method of making a functionally graded carbide body, comprising:
obtaining a group 5 metal carbide substrate having a bulk composition region comprising at least 70 wt% of a rhombohedral ζ -phase carbide; and
treating a surface of the group 5 metal carbide substrate with a carbon-containing gas at a carburization temperature to form a γ -phase-rich region having a γ -phase-rich composition region and a phase composition gradient region transitioning from the γ -

phase-rich composition region at the surface to the bulk composition region at a gradient depth below the surface.

18. The method of claim 17, wherein obtaining includes forming the group 5 metal
5 carbide substrate by:

assembling a particulate mixture of a group 5 metal source powder and a carbon
source powder; and

sintering the particulate mixture to form the group 5 metal carbide substrate
having the bulk composition region comprising at least 70 wt% of the rhombohedral ζ -
10 phase carbide.

19. The method of claim 18, wherein the group 5 metal source powder is a metallic group
5 metal powder or a group 5 metal hydride powder, and wherein the carbon source
powder is a γ -phase group 5 metal carbide powder.

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20. The method of claim 18, wherein the particulate mixture is selected from the group
consisting of: a mixture of a tantalum source powder and a carbon source powder, the
mixture having a carbon to tantalum atomic ratio of about 0.64 to about 0.68; a mixture of
a niobium source powder and a carbon source powder, the mixture having a carbon to
20 niobium atomic ratio of about 0.67 to about 0.68; and a mixture of a vanadium source
powder and a carbon source powder, the mixture having a carbon to tantalum atomic ratio
of about 0.61 to about 0.62.

21. The method of claim 18, wherein the sintering is performed at a sintering temperature
25 from about 1350 °C to about 1900 °C.

22. The method of claim 17, wherein the carburization temperature is from about 1270 °C
to about 1500 °C.

23. The method of claim 17, wherein treating the surface is performed for a carburization
time from about 10 hours to about 50 hours.

24. The method of claim 17, wherein the carbon-containing gas is a mixture comprising hydrogen and methane.

25. The method of claim 17, further comprising annealing the functionally graded carbide
5 body in a non-carbon-containing atmosphere at an annealing temperature below the carburization temperature to partially decarburize the surface.

26. The method of claim 25, wherein the annealing is performed for an annealing time
10 sufficient to produce a carbon to group 5 metal atomic ratio of about 0.8 at the surface.

27. The method of claim 17, further comprising milling the group 5 metal carbide
substrate to desired final dimensions of the functionally graded carbide body before
treating the surface with the carbon-containing gas.

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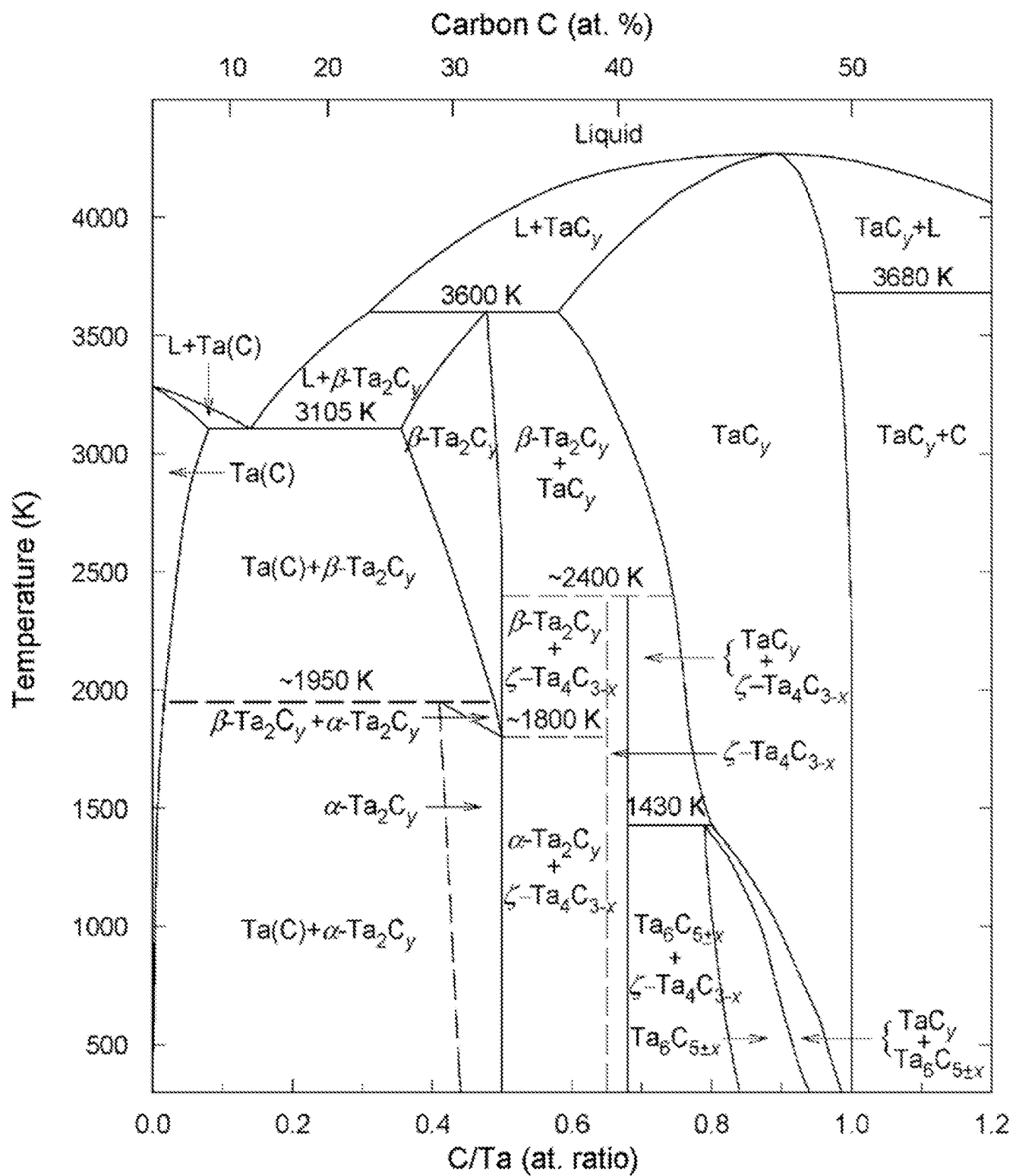


FIG. 1

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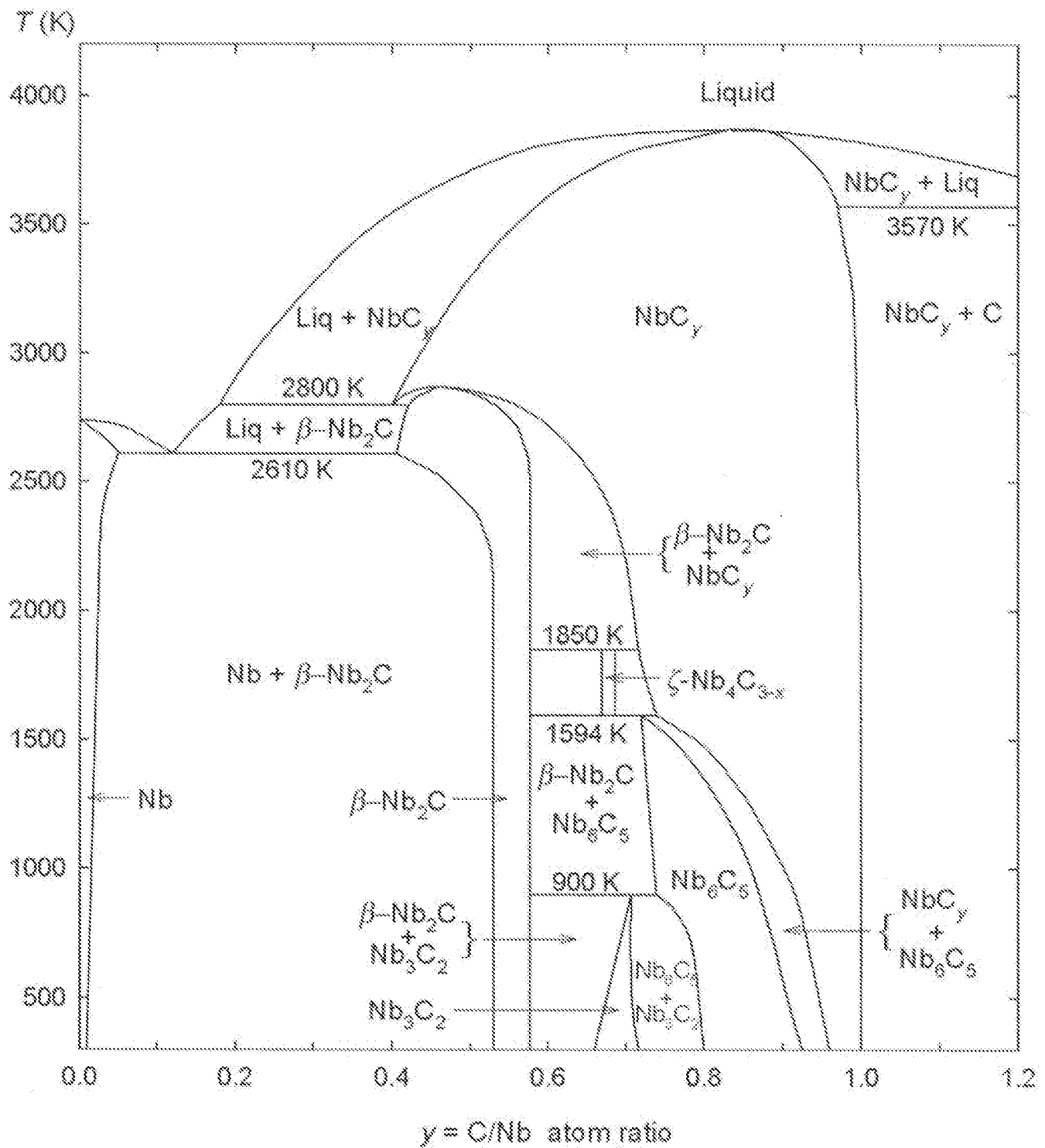


FIG. 2

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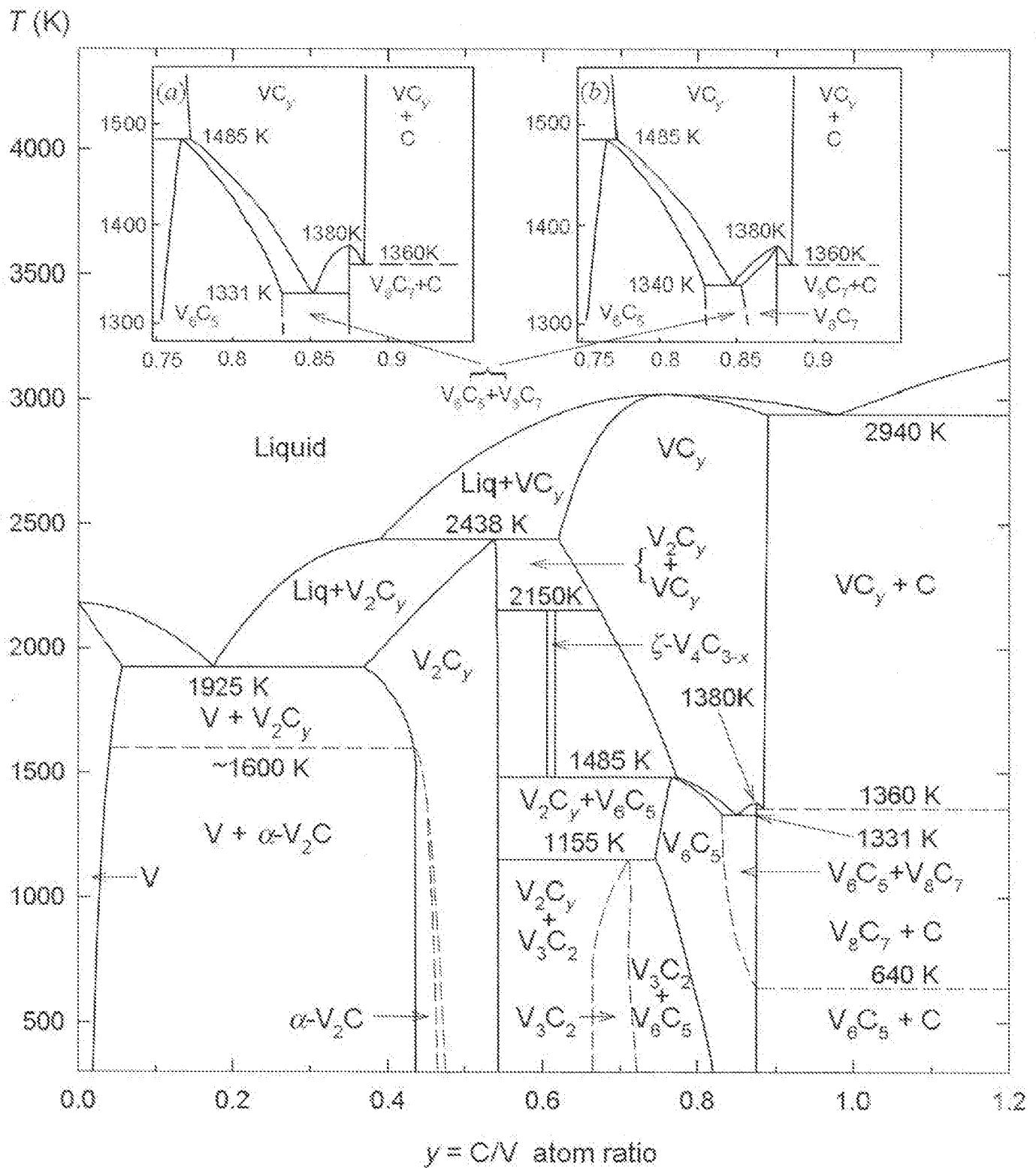


FIG. 3

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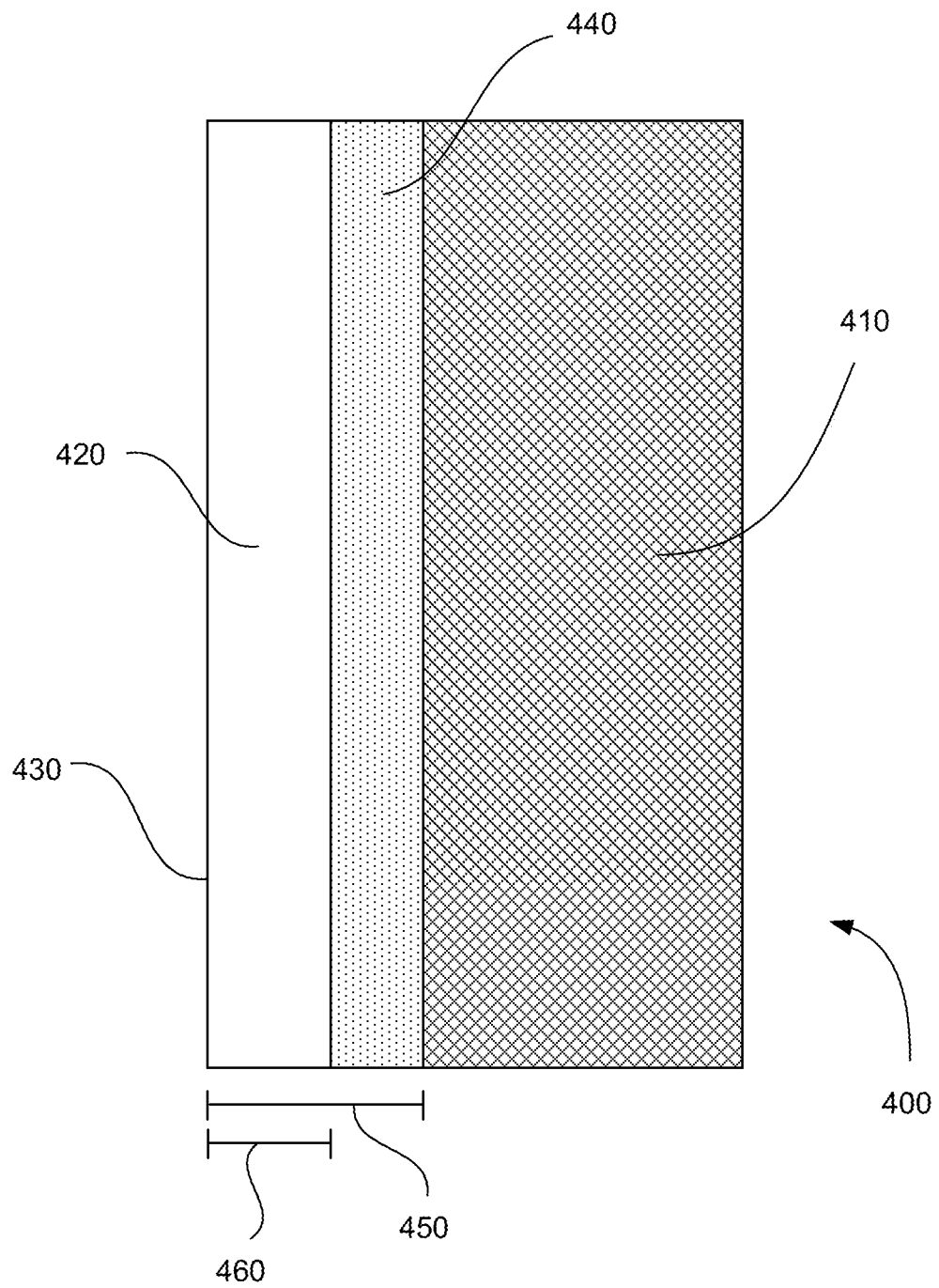


FIG. 4

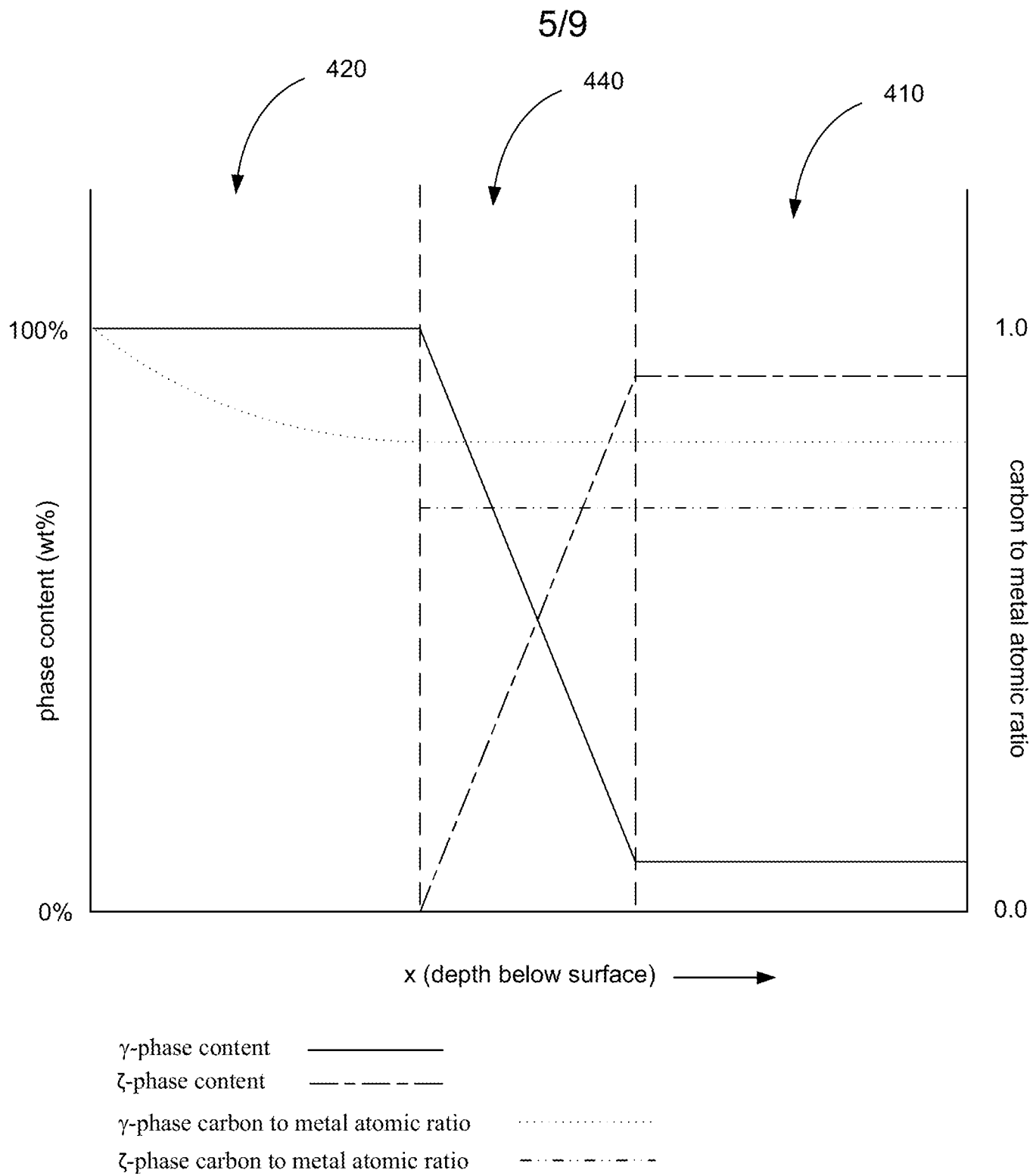


FIG. 5

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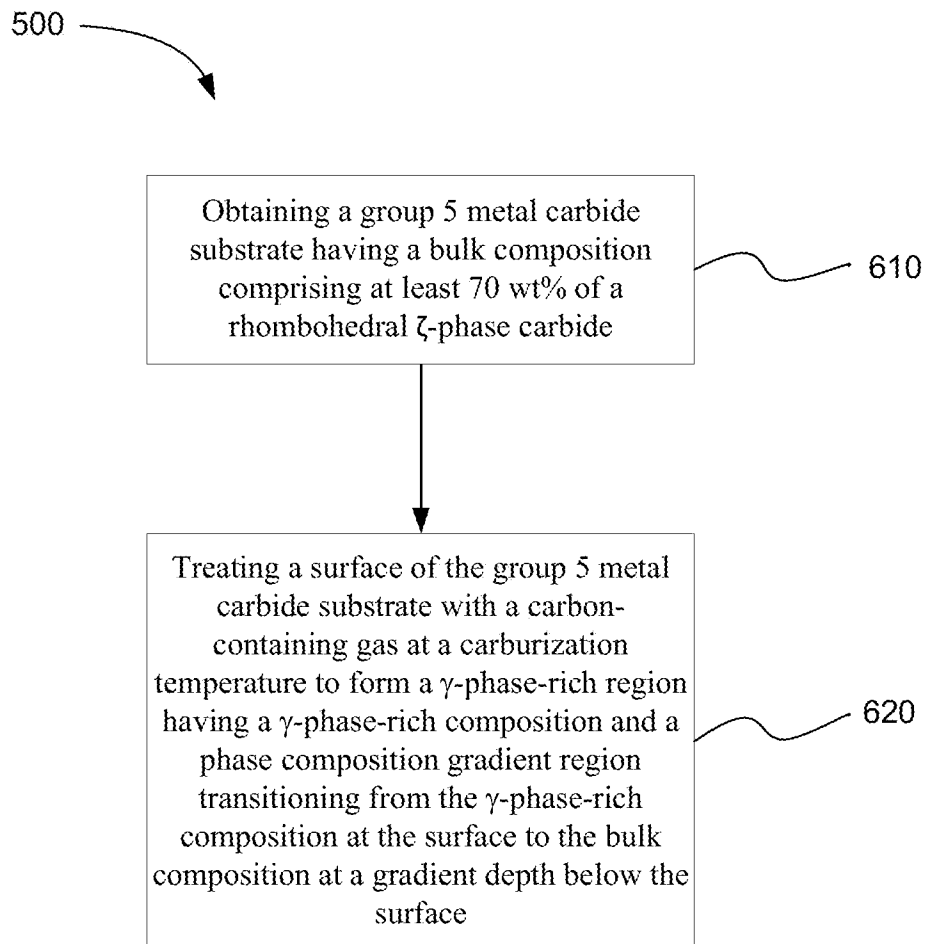


FIG. 6

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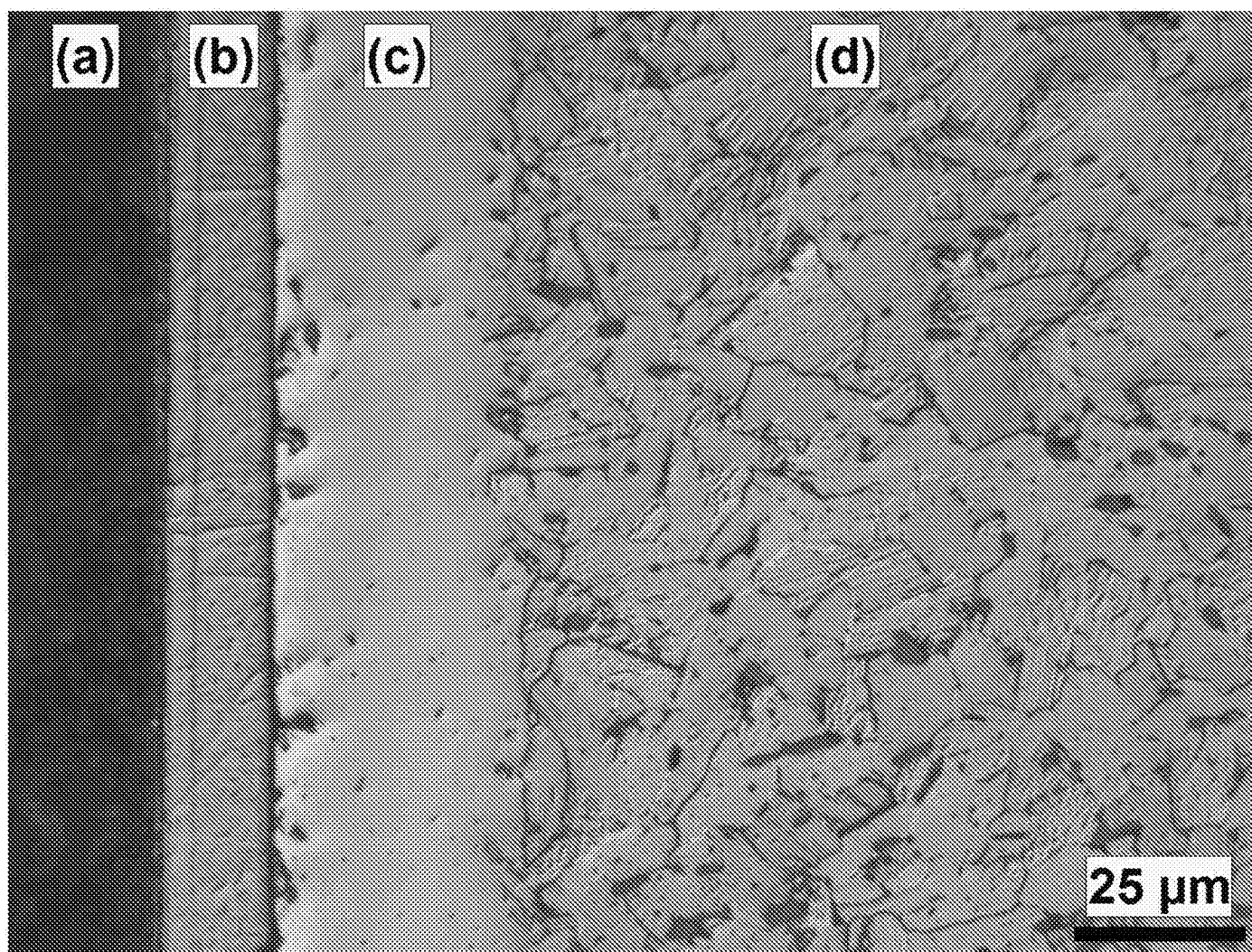


FIG. 7

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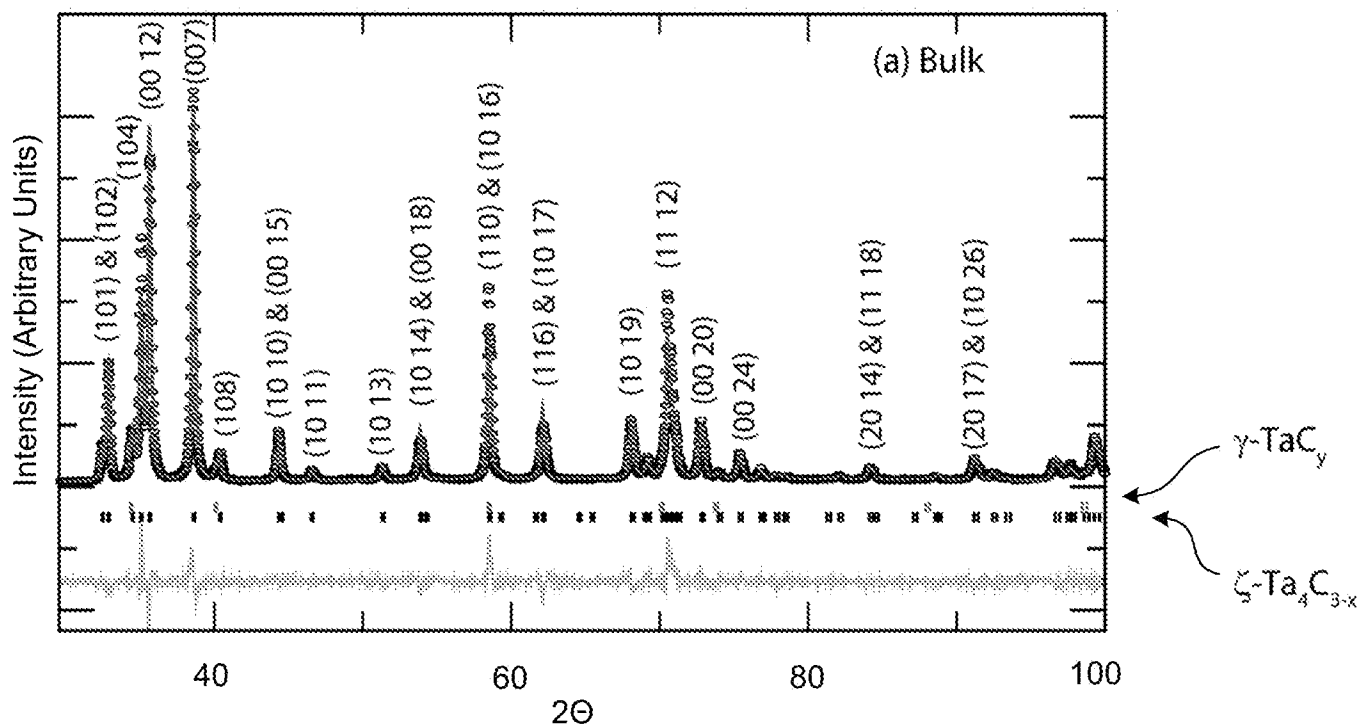


FIG. 8

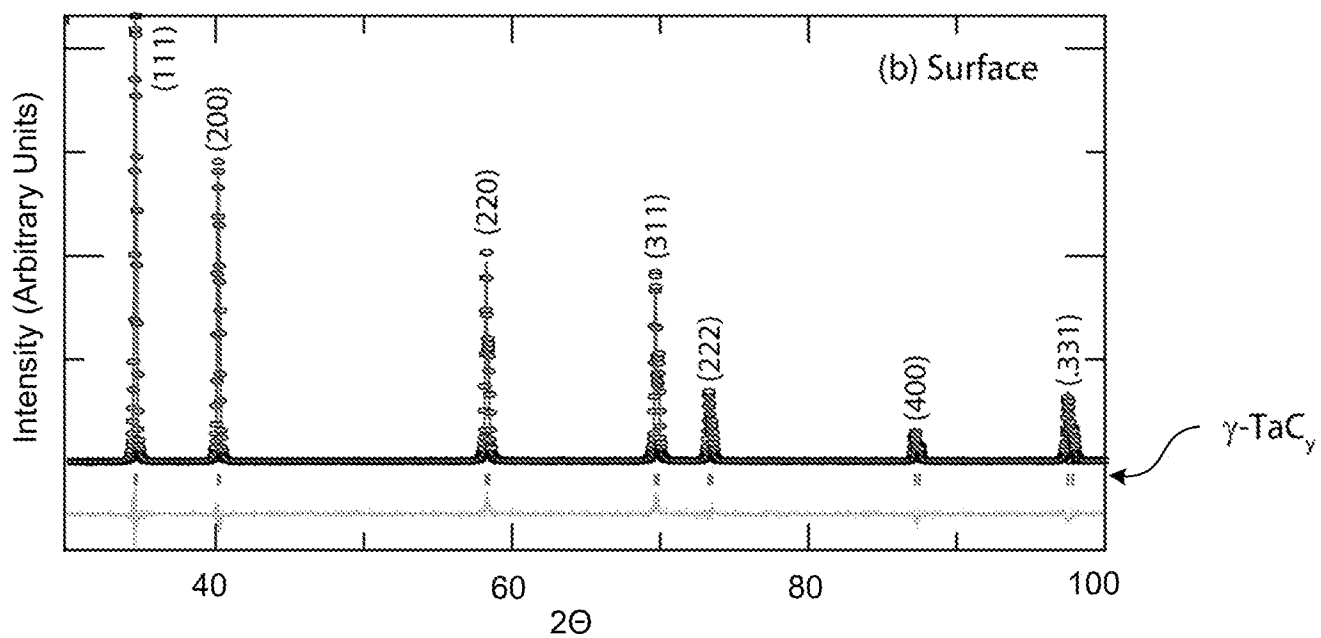


FIG. 9

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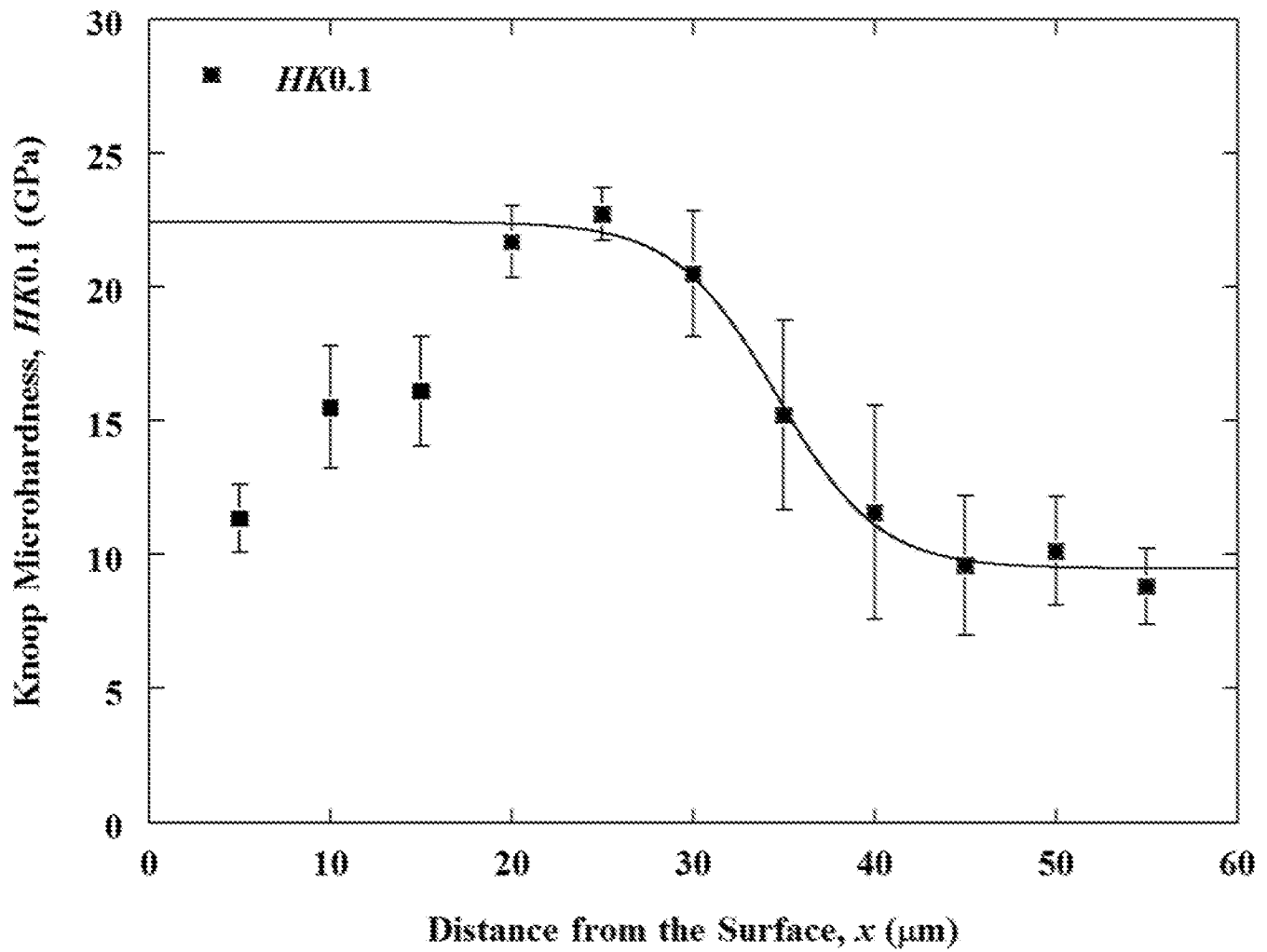


FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 16/14552

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B32B 15/04, C22C 27/02, C22C 29/02, C22C 45/10, C30B 21/02 (2016.01)

CPC - B32B 15/04, C22C 27/02, C22C 29/02, C22C 45/10, C22C 32/0084, C30B 21/02, C30B 29/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8)- B32B 15/04, C22C 27/02, C22C 29/02, C22C 45/10, C30B 21/02 (2016.01);

CPC- B32B 15/04, C22C 27/02, C22C 29/02, C22C 45/10, C22C 32/0084, C30B 21/02, C30B 29/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

USPC- 148/237, 148/278, 148/559, 148/561, 148/564;

Patents and NPL (classification, keyword; search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Pub West (US EP JP WO), Pat Base (AU BE BR CA CH CN DE DK EP ES FI FR GB IN JP KR SE TH TW US WO), Google Patent, Google Scholar, Free Patents Online; search terms: group, 5, V, vanadium, tantalum, niobium, Ta, Nb, alloy, carbide, phase, VC, TaC, NbC, graded, gradient, transition, density, rhombohedral, triangular, gamma, zeta

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2013/112217 A2 (CALIFORNIA INSTITUTE OF TECHNOLOGY) 01 August 2013 (01.08.2013), pg 3, para 3; pg 6, ln 3-4; pg 5, para 1; pg 5, para 7 to pg 6, para 3; pg 11, para 11 to pg 12, para 1; pg 13, para 1; pg 22, para 2	1-16
Y	GUSEV et al. "Atomic and vacancy ordering in carbide zeta-Ta ₄ C _{3-x} (0.28<=x<=0.40) and phase equilibria in the Ta-C system." Journal of Solid State Chemistry [online], 2007 [Retrieved on 2016-03-12], volume 180, pp. 3234-3246, Retrieved from the Internet: <doi: 10.1016/j.jssc.2007.09.015>, Figs. 7, 8; pg 3243, col 2, para 2 to pg 3244, col 1, para 1; pg 3245, col 1, para 2	1-16
Y	US 5,190,890 A (PRECHT et al.) 02 March 1993 (02.03.1993), col 4, ln 52 to col 5, ln 2; col 7, ln 52 to col 8, ln 33; col 9, ln 60 to col 10 ln 68; col 13, ln 47-58	4, 5, 8-10
Y	US 2011/0287923 A1 (SHETTY et al.) 24 November 2011 (24.11.2011), para [0004]-[0060]	1-16
Y	US 4,752,456 A (YODA et al.) 21 June 1988 (21.06.1988), col 2, ln 60 to col 15, ln 44	1-16

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

10 May 2016

Date of mailing of the international search report

03 JUN 2016

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

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PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 16/14552

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: Claims 1-16, drawn to a functionally graded carbide body of a group 5 metal carbide.

Group II: Claims 17-27, drawn to a method of making a functionally graded carbide body.

-- Please See Supplemental Box --

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-16

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Continued from Box No. III, Observations where unity of invention is lacking,

The inventions listed as Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features

Group II does not require a gamma-phase-rich region having a gamma-phase-rich composition at a surface of the carbide body, as required by Group I.

Group I does not require a method of making, comprising treating a surface of the group 5 metal carbide substrate with a carbon-containing gas at a carburization temperature to form a gamma-phase-rich region having a gamma-phase-rich composition region, as required by Group II.

Shared Common Features

The only feature shared by Groups I and II that would otherwise unify the groups is a functionally graded carbide body of a group 5 metal carbide, comprising: a bulk composition region comprising at least 70 wt% of a rhombohedral zeta-phase carbide of the group 5 metal carbide; and a phase composition gradient region transitioning from the gamma-phase-rich composition region to the bulk composition region at a gradient depth below the surface. However, this shared technical feature does not represent a contribution over prior art, because the shared technical feature is obvious over WO 2013/112217 A2 (California Institute of Technology), in view of the article entitled "Atomic and vacancy ordering in carbide zeta-Ta₄C₃-x (0.28≤x≤0.40) and phase equilibria in the Ta-C system" to Gusev, et al. (hereinafter 'Gusev'), (Journal of Solid State Chemistry 180 (2007) 3234-3246, doi:10.1016/j.jssc.2007.09.015),

California Institute of Technology discloses a functionally graded carbide body of a group 5 metal carbide (pg 3, para 3; pg 6, para 3-4), comprising: a bulk composition region of a group 5 metal carbide; and a phase composition gradient region transitioning from a composition region to the bulk composition region at a gradient depth below the surface comprising at least 70 wt% of a phase carbide (pg 5, para 1; pg 6, para 3; pg 11, para 11 to 12, para 1; pg 13, para 1, gradient transitions from metal such as Ta to carbide... amorphous metal to crystalline... using phase diagrams... with gradient compositions from 1% to 100% applied to a substrate.); but does not specifically disclose said bulk composition region comprising a rhombohedral zeta-phase carbide and a gamma-phase-rich composition region. However, Gusev discloses a rhombohedral zeta-phase carbide and a gamma-phase-rich composition region (Figs. 7, 8; Abstract; pg 3243, col 2, para 2 to pg 3244, col 1, para 1; pg 3245, col 1, para 2). To a person of ordinary skill in the art, it would have been obvious to substitute the carbide phases as taught by Gusev for use in the functionally graded carbide body as in California Institute of Technology in order to form desired properties using group 5 metals carbides for use in structural components (California Institute of Technology: pg 5, para 7 to pg 6, para 2), because California Institute of Technology and Gusev are directed towards methods of forming group 5 carbide materials using phase diagrams.

As the technical features were known in the art at the time of the invention, this cannot be considered a special technical feature that would otherwise unify the groups.

Groups I and II therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.