United States Patent Office

3,703,368
Patented Nov. 21, 1972

3,703,368

METHOD FOR MAKING CASTABLE CARBONITRIDE ALLOYS

Erwin Rudy, Beaverton, Oreg., assignor to Teledyne Industries, Inc., Los Angeles, Calif.

No Drawing. Filed Nov. 3, 1970, Ser. No. 89,222
Int. Cl. C22c *15/00*
U.S. Cl. 75—175.5 **19 Claims**

ABSTRACT OF THE DISCLOSURE

A method for fabricating improved cast refractory tooling materials is disclosed which comprises preparing a melt of titanium-tungsten-carbon-base alloy compositions $(Ti_xW_{1-x})C_z$, or titanium-tungsten-nitrogen-carbon base alloy compositions $(Ti_xW_{1-x})(N_yC_{1-y})_z$ under a nitrogen-containing atmosphere, in which the mole fraction x is variable between the limits 0.25 and 0.70, the mole fraction y is less than 0.50, the stoichiometry parameter z, which measures the combined gramatoms of nitrogen and carbon present per gramatom metal in the alloy, is variable between 0.25 and 0.45, and rapidly cooling the melt to form a carbonitride-metal alloy composite having a fine-grained microstructure consisting of a refractory, hard carbonitride phase and a metal phase, with the metal phase being rich in tungsten and contributing toughness to the composite and the carbonitride phase having titanium as its base metal.

The present invention relates to carbonitride alloys and more particularly to a method of making carbonitride alloys which, due to their physical characteristics, are particularly useful as machine tools.

Probably the most common material used as machine tools today is sintered carbide of one form or another. Commercial sintered carbide tooling material usually consists of a hard carbide alloy, usually tungsten and titanium carbide, dispersed in a matrix or binder of an iron group metal, usually cobalt or nickel. The binder provides toughness to the brittle carbide and also serves as a sintering aid during fabrication. However, the iron group metals have relatively low melting temperatures and the loss of strength of the binder alloys based on these metals at relatively low temperatures can cause thermal deformation and thermal wear to become the predominate wear mechanism at high cutting speeds and can cause premature failure of the tools.

To improve on these shortcomings of the iron metal bonded carbides, it has been proposed that sintered monocarbide alloys bonded by refractory metal alloys to be used as machine tools. However, due to low strength and poor mechanical shock resistance, these compositions are not competitive with conventional sintered carbides. In a more recent development refractory metal bonded castable carbide alloys were developed which showed a noted improvement over the sintered carbides when used as machine tools. The absence of thermal deformation under high thermal loads and the good wear resistance of these alloys cause them to be a superior material for tooling purposes.

It has now been discovered that an even superior tooling material can be provided by bonding carbonitride alloys with refractory metal alloys. Such a tooling material is disclosed and claimed in my United States patent application Ser. No. 86,622, filed concurrently with this application.

It is accordingly an object of the present invention to provide an improved method for making material for use as machine tooling material.

It is another object of the present invention to provide

an improved method for making a carbonitride alloy for use as a machine tooling material.

It is yet another object of the present invention to provide an improved method for making a composition of material comprising a carbonitride alloy bonded to a refractory metal alloy.

Briefly stated, and in accordance with the presently preferred embodiments of the invention, improved cast refractory tooling materials are fabricated by a method comprising preparing a melt of titanium-tungsten-carbon-base alloy compositions $(Ti_xW_{1-x})C_z$, or titanium-tungsten-nirtogen-carbon-base alloy compositions

$$(Ti_xW_{1-x})(N_yC_{1-y})_z$$

under a nitrogen-containing atmosphere, in which the mole fraction x is variable between the limits 0.25 and 0.70, the mole fraction y is less than 0.50, the stiochiometry parameter z, which measures the combined gramatoms of nitrogen and carbon present per gramatom metal in the alloy is variable between 0.25 and 0.45, and rapidly cooling the melt to form a carbonitride-metal alloy composite having a fine-grained microstructure consisting of a refractory, hard carbonitride phase and a metal phase, with the metal phase being rich in tungsten and contributing toughness to the composite and the carbonitride phase having titanium as its base metal.

DESCRIPTION OF THE PRODUCT FORMED BY THE INVENTION

The alloys of the invention are based on Group IV metal (titanium, zirconium and hafnium)-rich carbonitride alloys (relative Group IV metal content in excess of 60 atomic percent) bonded by Group VI metal (molybdenum and tungsten)-rich refractory metal alloys (relative Group VI metal content in excess of 80 atomic percent).

As is discussed in greater detail below, the desired microstructure of the composition, which consists of a fine-grained aggregate of carbonitride and metal phase, is obtained through rapid solidification of eutectic or near-eutectic alloys formed between the metal and the carbonitride phase. The lamellar, eutectic-type structure consists of the carbonitride phase, which is responsible for the cutting action, and the metal alloy, which contributes toughness and strength to the composite. In one desired composition a hypereutectic composition of the carbonitride metal is provided in which grains of primary carbonitride are dispersed throughout the lamellar eutectic structure. The presence of the primary carbonitride phase significantly improves the performance of the composite when employed as a machine tool. In another composition, the carbonitride metal composite comprises a fine-grained lamellar structure consisting of a tungsten-rich metal binder alloy and a carbonitride phase having titanium as its base metal. The carbonitride phase is a solid solution between isomorphous monocarbides and mononitrides. The molar ratio of nitrogen to carbon in the carbonitride phase can be varied at will but as is discussed below, for reasons related to fabricability and performance of the alloys, is usually kept below 0.40.

These carbonitride alloys are made possible by the existence of pseudobinary eutectic equilibria between the metal and the mononitride phases in the boundary systems titanium-tungsten-nitrogen, zirconium-tungsten-nitrogen and hafnium-tungsten-nitrogen, and the existence of nearly isothermally solidifying, eutectic-type equilibria between the carbonitride and the metal solid solutions in the systems titanium-tungsten-carbon-nitrogen, zirconium-tungsten-carbon-nitrogen and hafnium-tungsten-carbon-nitrogen. The phase equilibria in the metal-rich regions of the nitride and carbonitride systems are such, that over a wide range of metal-exchanges and temperatures, Group

IV metal-rich carbonitride, or nitride, solid solutions are in equilibrium with tungsten-rich metal alloys. Within the range of alloy compositions found useful in machine tool applications, the products of the eutectic crystallization consist of tungsten-rich binder alloys (relative tungsten content in excess of 80 atomic percent) and a Group IV metal-rich carbonitride alloy (relative Group IV metal content in excess of 60 atomic percent).

The nitrogen dissociation pressures of only nitride-containing alloys located within the range where suitable binder alloys are formed, are too high at melting temperatures to be of practical use. However, the nitrogen partial pressures as well as the eutectic temperatures are substantially lowered by alloying the nitrides with carbides. Thus, for instance, at a carbon to nitrogen molar ratio of 1:1 and a nitrogen pressure of 1 atmosphere, eutectic solidification occurs at approximately 2750° C. along the join metal+carbonitride, at which the metal phase consists of a 94 atomic percent tungsten, 6 atomic percent titanium-alloy, and the interstitial alloy of almost pure titanium carbonitride. By comparison, TiN in contact with a 10 atomic percent titanium-90 atomic percent tungsten metal alloy melts at 2970° C. and the mixture has at this temperature a decomposition pressure of approximately 6 atmospheres.

The behavior of the other Group IV metal nitrides (ZrN, HfN) in systems with tungsten are generally similar to the titanium systems, except that the nitrogen decomposition pressures at equivalent temperatures and pressures are somewhat lower than in the titanium-based alloys. However, the eutectic temperatures in these systems are higher than in the titanium systems (3070° C. at the join ZrN-tungsten and 3100° C. at the join HfN-tungsten) and remain practically unchanged by alloying with carbon; additionally, the nitride or carbonitride content of the eutectic structure is lower than in the titanium systems, which results in substantially higher wear rates of zirconium and hafnium-based alloys in application as machine tools. The phase equilibria in the corresponding systems of Group IV metals with molybdenum, nitrogen, and carbon are generally similar to the tungsten systems, although the eutectic temperatures, and hence the nitrogen decomposition pressures, of the alloys in the melting range are substantially lower. The hard alloy content of the eutectics in the molybdenum-containing alloys and the strengths of molybdenum-rich alloy binders are too low, however, in order to be competitive with the tungsten-based alloys as machine tools.

Considering fabricability and performance, the preferred embodiment of the carbonitride-metal composite in applications as a machine tool is therefore based on the titanium-tungsten-carbon-nitrogen system. As is discussed below, certain improvements can be achieved by alloying with other elements, notably by partial substitution of titanium by zirconium or hafnium, and by small additions of Group V metals (vanadium, niobium and tantalum). Partial substitution of tungsten by molybdenum and rhenium is also possible.

The compositions of the alloys are conveniently expressed either in atomic percent of the constituent elements, for example as $Ti_uW_vC_wN_r$, $(u+v+w+r=100)$, where u, v, w and r are respectively, the atomic percent of titanium, tungsten, carbon and nitrogen present in the alloy; or as relative mole fractions of metal and interstitial elements in the form $(Ti_xW_{1-x})(N_yC_{2-y})_z$, whereby x and $1-x$ are, respectively, the relative mole fractions of titanium and tungsten, and y and $1-y$ are respectively, the relative mole fraction of nitrogen and carbon. The stoichiometry parameter z measures the combined number of moles of interstitial atoms of carbon and nitrogen per gramatom of metal titanium+tungsten. The latter method of defining the overall composition of the alloys is especially useful in defining concentration spaces of interstitial alloys of the type discussed here. The relationships between the two sets of concentration parameters, which

are interchangeably used throughout in the description of the alloys of the invention, are as follows:

$$u=100\cdot\frac{x}{1+z}\qquad v=100\cdot\frac{1-x}{1+z}$$

$$w=100\cdot\frac{y\cdot z}{1+z}\qquad r=100\cdot\frac{(1-y)z}{1+z}$$

$$x=\frac{u}{u+v};\qquad y=\frac{r}{w+r};\qquad z=\frac{w+r}{u+v}$$

The preferred compositions $(Ti_xW_{1-x})(C_yN_{1-y})_z$ of the base alloys extend between limits of x between 0.28 and 0.60, of y less than 0.50, and of z between 0.28 and 0.37. Alloys located outside the preferred range, but inside the boundaries defined by limits of x between 0.25 and 0.70, of y less than 0.50, and of z between 0.25 and 0.45, are less suitable for machine tools but are acceptable for some applications.

Within the area of the preferred compositions, carbonitride-metal composites with low interstitial element contents consist of eutectic only and exhibit somewhat higher wear rates than hypereutectic alloys which contain excess primary carbonitride. Castability, however, becomes poor if the carbon plus nitrogen content of the alloys exceeds about 28 atomic percent ($z>0.39$). Machine tools fabricated from such alloys are also more prone to edge-chipping than tools fabricated from the tougher eutectic, or slightly hypereutectic, alloys. The optimum interstitial element contents of the carbonitride-metal composites when applied as machine tools are between 25 and 26.5 atomic percent ($z=0.33$ to 0.36).

For a given titanium to tungsten ratio and fixed total carbon plus nitrogen content, increased substitution of nitrogen by carbon increases the hardness of the composites, with overall performance reaching a maximum of nitrogen to carbon molar ratios

$$\left(\frac{y}{1-y}\right)$$

between 0.03 and 0.20. It is especially noteworthy that the top cratering rate of tools made with the composition of the present invention is almost cut in half by substitution of only small amounts ($y=0.02$) of nitrogen in carbide alloys, while improvements in flank wear range between 0 and 50%. At fixed total interstitial carbon plus nitrogen content and fixed molar ratios of nitrogen to carbon, top cratering resistance improves with increasing titanium to tungsten-ratios

$$\left(\frac{x}{1-x}\right)$$

in the alloys, while flank wear is only moderately affected by the relative metal exchange. Edge stability in heavy roughing applications is optimum at titanium exchanges corresponding to $x\sim0.35$ (at $z=0.34$), decreases slightly for alloys with values of x between 0.35 and 0.50, and drops sharply towards higher titanium contents.

Maximum attainable molar ratios of nitrogen to carbon in the alloys at casting temperatures are a function of the metal exchange as well as the nitrogen pressure in the gas phase. For a nitrogen pressure of 1 atmosphere, a combined interstitial content corresponding to $z=0.33$ to 0.35, values for these ratios are listed in Table 1 below. These ratios become smaller if the nitrogen pressure is reduced, and are larger than the values listed in Table 1 if the nitrogen pressure is increased over 1 atmosphere.

TABLE 1

Maximum molar ratios of nitrogen to carbon in titanium-tungsten-carbon-nitrogen melts. Data based on one atmosphere nitrogen pressure, a combined nitrogen and carbon content of 25 atomic percent, and 150° C. superheating of the melt.

Molar ratio Ti:W in the alloy:[1]	Maximum molar ratio N:C in the melt [2]
0.59	0.05
0.66	0.11
0.78	0.25
0.92	0.67
1.04	1.50

[1] $\frac{x}{1-x}$

[1] $\frac{y}{1-y}$

Undesirable side reactions, such as the formation of W_2C and WC, can occur in unfavorably selected alloy compositions and nitrogen pressures, but can be avoided if a certain minimum nitrogen content in the carbonitride alloys is maintained for a given metal exchange and given melting conditions.

METHOD OF MAKING THE COMPOSITIONS

In accordance with the present invention, the alloys may, for example, be prepared by arc (skull) melting in a nonconsumable electrode arc furnace, or by plasma arc melting, and casting of the melt in water cooled molds, or molds made of refractory materials, preferably graphite. The nitrogen in the compositing may be furnished either by providing it directly in the melts, such as by adding TiN to the melt, or it may be furnished from a nitrogen-containing atmosphere above the melt. Aside from the desirability for a certain nitrogen pressure in the furnace atmosphere to maintain the desired nitrogen to carbon balance in the alloys, arc melting under pure nitrogen caused less electrode wear and resulted in more stable arcs than arc melting under noble gases such as helium and argon. This also represents an economic advantage in fabricating the tools. The partial pressure of the nitrogen in the nitrogen-containing atmosphere is preferably maintained at a value less than four atmospheres. For reasons not well understood at the present time, cracking of the cast parts during cooling also appeared substantially reduced for the alloys which were melted under nitrogen. Induction melting of the composites in a lower frequency induction furnace (1000 to 2000 Hz.), using graphite as container material, plasma arc melting, and direct resistance melting is also possible.

Centrifugal casting of the melt is preferable to casting techniques employing stationary molds, because the former technique minimizes the problems associated with the formation of shrinkage pipes, allows higher casting speeds, and also permits the development of processes by which multiple dies can be used to cast parts closely to shape. Dense bodies can also be prepared by powder-metallurgical techniques, using premelted and then comminuted alloy stock. The performance of sintered alloys as machine tools, however, is inferior to the performance of the cast alloys.

It is important in whatever manner of fabrication that is employed, that the eutectic or near-eutectic melts of the alloys of the invention be solidified under a high temperature gradient (preferably above 20° C./sec.) in order to assure the formation of the fine-grained structure necessary to obtain composites with optimum mechanical properties and performance as machine tools. It has been observed that solidification under higher temperature gradients causes a finer-grained structure and, conversely, solidification under lower temperature gradients causes a coarser-grained structure.

POSSIBLE MODIFICATIONS IN THE PREFERRED COMPOSITIONS

The quaternary alloys of the base alloy system can be extensively modified by alloying additions of other metals

or interstitials without changing their principal characteristics. A correlation between amount and type of alloying additions, and performance of the resulting composites as machine tools, indicates that noticeable improvements can be achieved by certain low level alloying additions to the base alloys, but that higher level (above 5 atomic percent) alloying is generally unnecessary or even undesirable; addition of selected elements up to certain concentrations proved inert while others resulted, even at low concentrations, in a substantial drop of the cutting performance. The summary of the effect of alloying additions to titanium-tungsten-carbon-nitrogen-based alloys given below is based on the performance of the carbonitride-metal composites in cutting annealed 4340 steel.

(1) Molybdenum, substituted in amounts up to 10 atomic percent of tungsten in the base alloy system, resulted in no noticeable change in performance, although castability appeared impaired at concentrations higher than 5 atomic percent. Exchanges of 50 atomic percent resulted in nose breakdown and chip welding under the chosen test conditions.

(2) 10 atomic percent chromium in replacement for tungsten resulted in poor castability due to preferential vaporization of chromium in the arc and also caused an increased in brittleness of the composites. The maximum tolerable limit without impairing performance was placed at 3 atomic percent.

(3) Rhenium in amounts up to 15 atomic percent in replacement for tungsten improves the cracking resistance of the composites, but had no measurable effect on cutting performance.

(4) Zirconium and hafnium, substituted in amounts up to 5 atomic percent for titanium in the base alloys, improved tool life, while concentrations in excess of 15 atomic percent adversely affected tool performance.

(5) Low level additions (below 5 atomic percent) of Group V metals (vanadium, niobium and tantalum) in exchange for titanium were essentially inert, whereas concentrations in excess of 10 atomic percent resulted in cracking of the casting and edge-chipping of the tools.

(6) Boron in amounts up to 3 atomic percent in replacement for carbon or nitrogen entered substitutionally into the carbonitride solid solution and had no adverse effect on the cutting performance.

(7) Oxygen in amounts up to 4 atomic percent in replacement for carbon or nitrogen results in reduced friction and welding tendency, at some sacrifice in strength and cracking resistance.

(8) Additions of 1 to 5 atomic percent of a number of elements, including iron, nickel, copper, manganese, and aluminum to the tool batches prior to melting did not produce any adverse effects on tool performance.

SPECIFIC EXAMPLES OF THE INVENTION

Example I

An alloy with the initial composition $Ti_{37}W_{38}C_{18}N_7$ was arc melted in a graphite-skull under 1 atmosphere nitrogen pressure and then drop-cast into a graphite mold. Analysis of the cast tool blank indicated a nitrogen pick-up of 2 atomic percent from the gas atmosphere. Metallographic examination revealed substantial amounts of primary carbonitride phase dispersed in a matrix of bivariantly solidified metal+carbonitride eutectic. The average lamellae spacing in the eutectic structure was less than 1 micron and the hardness was $R_A=88$.

Example II

An alloy with an initial composition $Ti_{37}W_{38}C_{14}N_{11}$ was prepared in the same manner as described in Example I, except that the nitrogen pressure in the furnace was kept at ¾ atmosphere. The nitrogen pickup from the gas atmosphere was negligible, and the microstructure showed moderate amounts of primary carbonitride in addition to the eutectic. The hardness of the material was $R_A=87$.

Example III

An alloy $Ti_{22}Zr_1W_{52}C_{23}N_2$ was arc cast under ¾ atmosphere nitrogen and fabricated to shape in the same manner as described in Example I. Nitrogen pickup from the gas atmosphere during melting was between 0.5 and 1 atomic percent. The microstructure of the sample showed primary carbonitride phase in a matrix of a very fine-grained eutectic with an average lamellae spacing less than 0.5 micron. The hardness of the material was $R_A=86.6$.

Example IV

A metal-carbide alloy with the initial composition $Ti_{27}Zr_1W_{53}C_{19}$ was arc melted in a graphite skull and nitrided in the melted state by a 2 minute exposure to nitrogen at atmospheric pressure prior to casting. The nitrogen content of the alloys was 5 atomic percent, resulting in an approximate overall composition of the cast part corresponding to $Ti_{25}Zr_1W_{50}C_{19}N_5$.

Example V

An alloy $Ti_{21}Zr_1W_{48}C_{25}N_5$ was arc cast under 1 atmosphere nitrogen pressure as described in Example I. Post-experiment examination showed a total interstitial (carbon plus nitrogen) element content of 26.5 atomic percent, indicating a nitrogen loss of 3.5 atomic percent during melting. Hardness of the material was $R_A=88.3$.

Example VI

An alloy with the initial composition $Ti_{22}Zr_1W_{52}C_{25}$ contained, after arc casting under 1 atmosphere nitrogen pressure, 1.1 atomic percent nitrogen. The microstructure of the sample revealed primary carbonitride gains in a matrix of carbonitride+metal eutectic. The hardness of the tool was $R_A=87.5$.

Example VII

An alloy with the initial cimposition $Ti_{22}Zr_1W_{52}C_{25}$ had an analyzed nitrogen content of 2.3 atomic percent after arc melting and casting under 1 atmosphere nitrogen. The measured hardness was $R_A=87.0$.

While the invention is thus disclosed and several specific embodiments described in detail, it is not intended that the invention be limited to these shown embodiments. Instead, many modifications will occur to those skilled in the art which fall within the spirit and scope of the invention. It is intended that the invention be limited only by the appended claims.

What is claimed is:

1. A method of forming a carbonitride-metal alloy composition comprising the steps of:

preparing a melt comprising a Group IV metal-Group VI metal-nitrogen-carbon base alloy composition

$$[(\text{Group IV metal})_x(\text{Group VI metal})_{1-x}][N_yC_{1-y}]_z$$

in which said Group IV metal is comprised of at least 85 atomic percent titanium, said Group VI metal is comprised of at least 90 atomic percent tungsten, and in which the mole fraction x is variable between the limits 0.25 and 0.70, the mole fraction y is less than 0.50, and the stoichiometry parameter z, which measured the combined number of moles of nitrogen and carbon per gramatom metal alloy, is variable between the limits 0.25 and 0.45; and

cooling said melt at a rate faster than 20° C. per second to form a carbonitride-metal alloy composite having a fine-grained, lamellar microstructure consisting of a refractory, hard carbonitride phase and a metal phase, with the metal phase being rich in said Group VI metal and contributing toughness to the composite and said carbonitride phase having said Group IV metal as its base metal.

2. The method of claim **1** wherein said Group VI metal comprises at least 90 atomic percent tungsten and up to 10 atomic percent molybdenum.

3. The method of claim **1** wherein said Group VI metal comprises at least 97 atomic percent tungsten and up to 3 atomic percent chromium.

4. The method of claim **1** wherein said Group VI metal comprises at least 90 atomic percent tungsten and up to 10 atomic percent rhenium.

5. The method of claim **1** wherein said Group IV metal comprises at least 85 atomic percent titanium and up to 15 atomic percent selected from the group consisting of zirconium and hafnium.

6. The method of claim **1** in which said melt comprises a Group V metal-titanium-tungsten-carbon-nitrogen base alloy composition $(M_vTi_{x-v}W_{1-x})(N_yC_{1-y})_z$, in which M is a Group V metal selected from the group consisting of vanadium, niobium and tantalum, the mole fraction v is less than 0.05, the mole fraction x is variable between the limits 0.25 and 0.70, the mole fraction y is less than 0.50, and the stoichiometry parameter z, which measures the combined number of moles of nitrogen and carbon per gramatom metal alloy, is variable between the limits 0.25 and 0.45.

7. The method of claim **1** in which said melt comprises a titanium-tungsten-carbon-nitrogen-boron base alloy composition $(Ti_xW_{1-x})(B_uN_yC_{1-u-y})_z$ in which the mole fraction x is variable between the limits 0.25 and 0.70, the mole fraction u is less than 0.03, the mole fraction y is less than 0.50, and the stoichiometry parameter z, which measures the combined number of moles of boron, nitrogen and carbon per gramatom metal alloy, is variable between the limits 0.25 and 0.45.

8. The method of claim **1** in which said melt comprises a titanium-tungsten-carbon-nitrogen-oxygen base alloy composition $(Ti_xW_{1-x})(O_tN_yC_{1-t-y})_z$, in which the mole fraction x is variable between the limits 0.25 and 0.70, the mole fraction t is less than 0.04, the mole fraction y is less than 0.50, and the stoichiometry parameter z, which measures the combined number of moles of oxygen, nitrogen and carbon per gramatom metal alloy, is variable between the limits 0.25 and 0.45.

9. The method of claim **1** in which said melt is prepared under a nitrogen-containing atmosphere.

10. The method of claim **9** in which the partial pressure of nitrogen in said nitrogen-containing atmosphere is less than four atmospheres.

11. A method of forming a carbonitride-metal alloy composition comprising the steps of:

preparing a melt comprising a Group IV metal-Group VI metal carbon base alloy composition

$$[(\text{Group IV metal})_x(\text{Group VI metal})_{1-x}]C_z$$

under a nitrogen containing atmosphere, in which said group IV metal is comprised of at least 85 atomic percent titanium, said Group VI metal is comprised of at least 90 atomic percent tungsten, and in which the mole fraction x is variable between the limits 0.25 and 0.70, and the stoichiometry parameter z, which measured the number of moles of carbon per gramatom metal alloy, is variable between the limits 0.25 and 0.45; and

cooling said melt at a rate faster than 20° C. per second to form a carbonitride-metal alloy composite having a fine-grained, lamellar microstructure consisting of a refractory, hard carbonitride phase and a metal phase, with the metal phase being rich in said Group VI metal and contributing toughness to the composite and said carbonitride phase having said Group IV metal as its base metal.

12. The method of claim **11** wherein said Group VI metal comprises at least 90 atomic percent tungsten and up to 10 atomic percent molybdenum.

13. The method of claim **11** wherein said Group VI metal comprises at least 97 atomic percent tungsten and up to 3 atomic percent chromium.

14. The method of claim **11** wherein said Group VI metal comprises at least 90 atomic percent tungsten and up to 10 atomic percent rhenium.

15. The method of claim **11** wherein said Group IV metal comprises at least 85 atomic percent titanium and up to 15 atomic percent selected from the group consisting of zirconium and hafnium.

16. The method of claim **11** in which said melt comprises a Group V metal-titanium-tungsten-carbon base alloy composition $(M_vTi_{x-v}W_{1-x})C_z$, in which M is a Group V metal selected from the group consisting of vanadium, niobium and tantalum, the mole fraction *v* is less than 0.05, the mole fraction *x* is variable between the limits 0.25 and 0.70, and the stoichiometry parameter *z*, which measures the number of moles of carbon per gramatom metal alloy, is variable between the limits 0.25 and 0.45.

17. The method of claim **11** in which said melt comprises titanium-tungsten-carbon-boron base alloy composition $(Ti_xW_{1-x})(B_uC_{1-u})_z$ in which the mole fraction *x* is variable between the limits 0.25 and 0.70, the mole fraction *u* is less than 0.03, and the stoichiometry parameter *z*, which measures the combined number of moles of boron and carbon per gramatom metal alloy, is variable between the limits 0.25 and 0.45.

18. The method of claim **11** in which said melt comprises a titanium-tungsten-carbon-oxygen base alloy composition $(Ti_xW_{1-x})(O_tC_{1-t})_z$, in which the mole fraction *x* is variable between the limits 0.25 and 0.70, the mole fraction *t* is less than 0.04, and the stoichiometry parameter *z*, which measures the combined number of moles of oxygen and carbon per gramatom metal alloy, is variable between the limits 0.25 and 0.45.

19. The method of claim **11** in which the partial pressure of nitrogen in said nitrogen-containing atmosphere is less than four atmospheres.

References Cited

UNITED STATES PATENTS

3,124,452	3/1964	Kraft	75—135
3,169,828	2/1965	Muta	23—191
3,492,100	1/1970	Roubin	23—315
3,528,808	9/1970	Lemkey	75—135 X
3,554,737	1/1971	Foster	75—134

L. DEWAYNE RUTLEDGE, Primary Examiner

J. E. LEGRU, Assistant Examiner

U.S. Cl. X.R.

75—134 F, 135, 176