PREPARATION OF LARGE CRYSTAL REFRACTORY METAL MONOCARBIDES

Filed Aug. 14, 1967 3 Sheets-Sheet 1

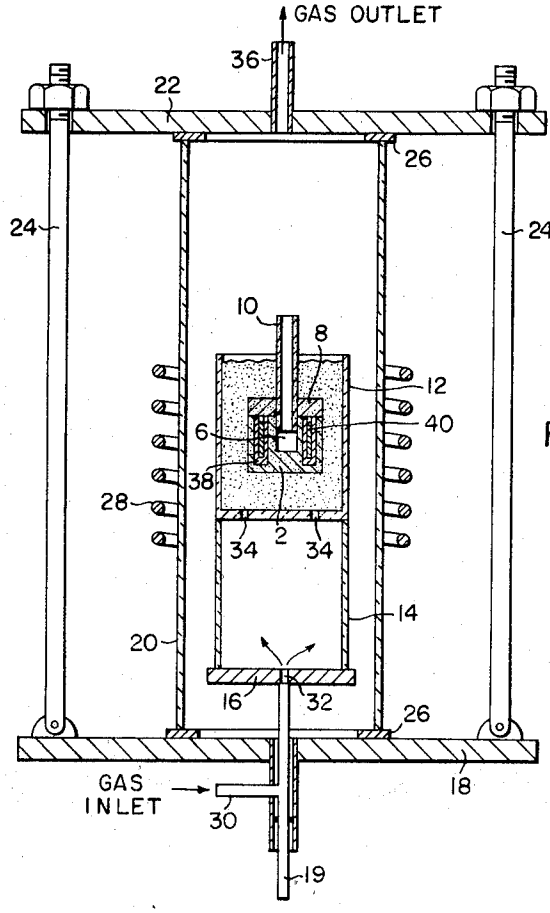


FIG. I.

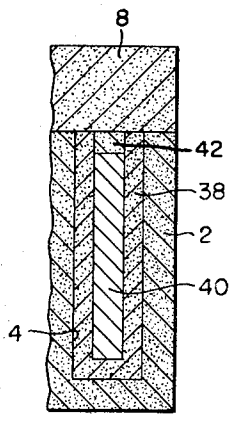


FIG. IA.

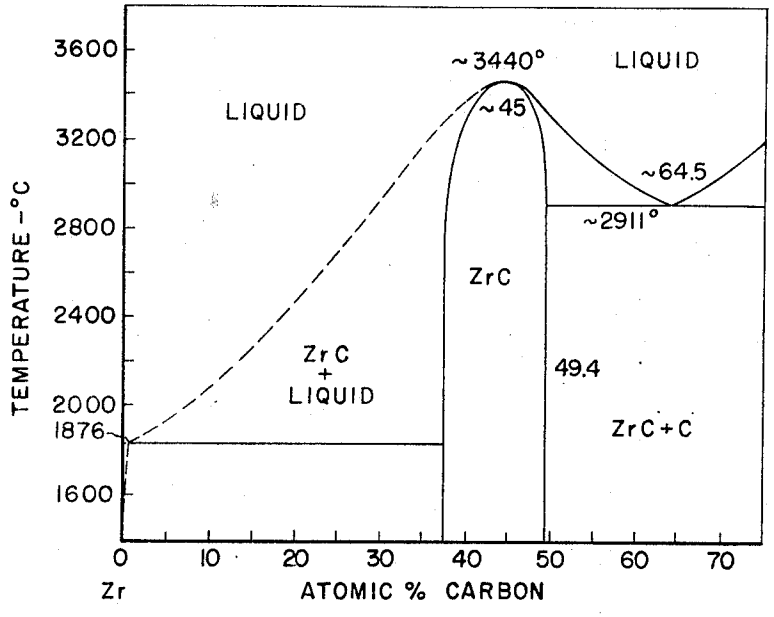


FIG. 2.

PREPARATION OF LARGE CRYSTAL REFRACTORY METAL MONOCARBIDES

Filed Aug. 14, 1967 3 Sheets-Sheet 2

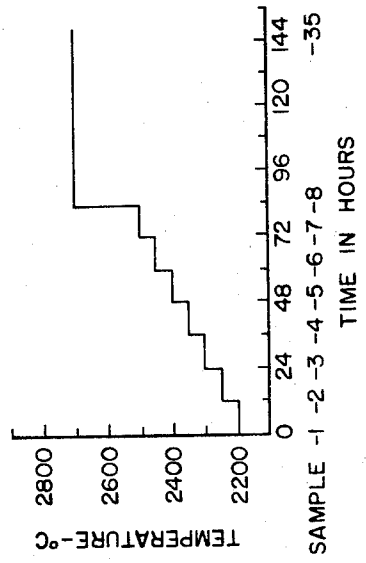


FIG. 3A.

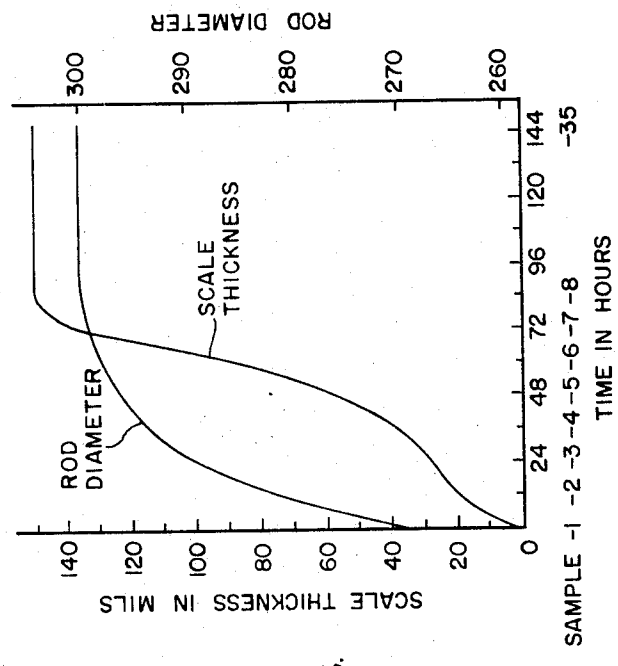
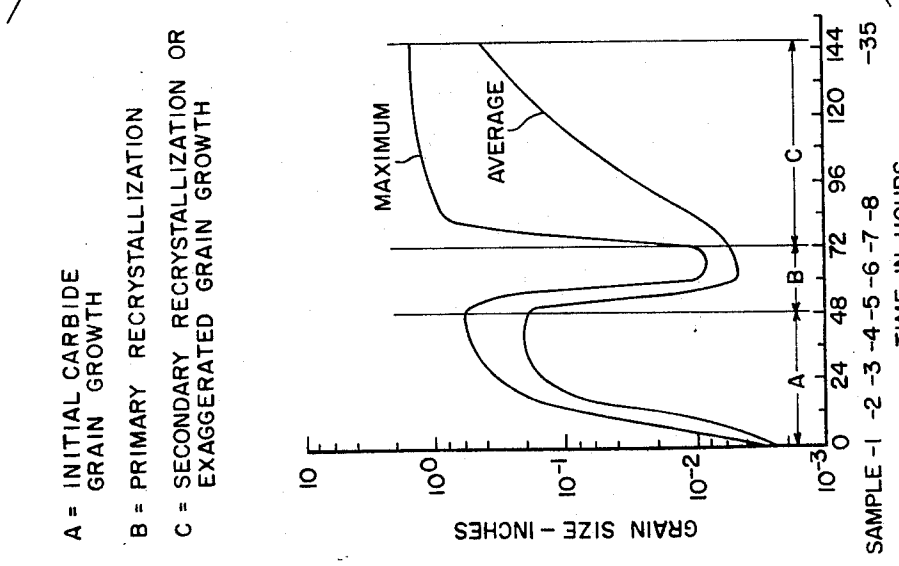


FIG. 3C.

FIG. 3B.



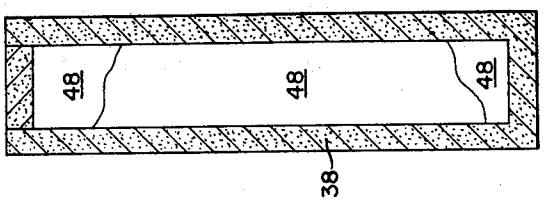


FIG.8.

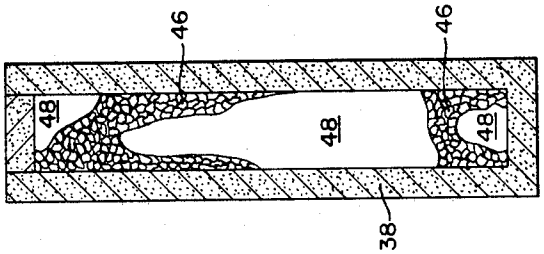


FIG.7.

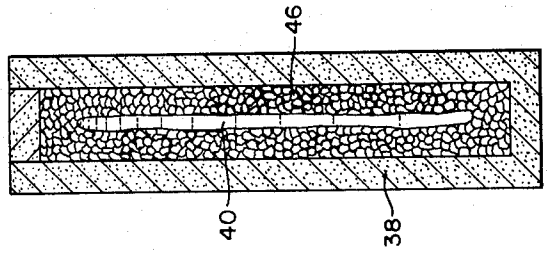


FIG.6.

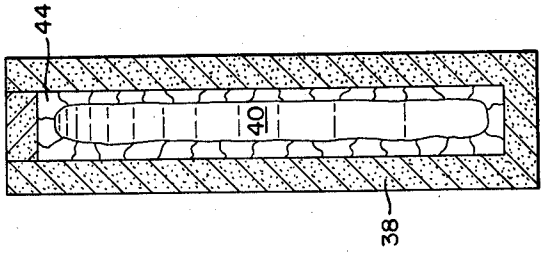


FIG.5.

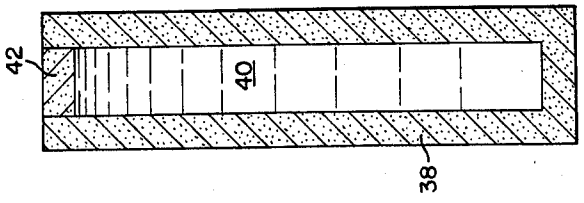


FIG.4.

United States Patent Office 3,507,616
Patented Apr. 21, 1970

3,507,616

PREPARATION OF LARGE CRYSTAL REFRACTORY METAL MONOCARBIDES

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U.S. Cl. 23—208 6 Claims

ABSTRACT OF THE DISCLOSURE

A method of growing a body comprising large secondarily recrystallized crystals of the full carbide of a metal of Groups IV–B and V–B of the Periodic Table wherein a body of at least one metal selected from the group consisting of Ti, Zr, Hf, V, Nb, and Ta, and alloys of two or more of these metals, disposed in contact with carbonaceous material capable of carburizing the metal, is heated at an elevated temperature in the range from above the melting point of the metal but not exceeding the metal carbide-carbon eutectic temperature of the metal for a period of time sufficient to cause formation of a full metal carbide of the entire body, and with the temperature being increased as carburization proceeds by diffusion so that a continually increasing outer wall of solid metal carbide forms and encloses a progressively diminishing pool of molten metal, the increased temperature causing expansion of the molten metal pool so that plastic strain is imposed on the enclosing metal carbide wall, and whereby to cause the initial formation of a primary small, grain structure in the metal carbide and then maintaining the carbide body at a high temperature for a period of time so that it subsequently secondarily recrystallizes into at least one large crystal structure. Relatively large bodies of the metal carbides comprised of a single crystal or only a few single crystal grains are obtained from the process.

CROSS REFERENCE TO RELATED APPLICATIONS

This invention is related to copending application Ser. No. 513,448 (now abandoned).

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a process for the growth of large secondary crystals of a monocarbide of a metal in a reproducible and controlled manner during and subsequent to the direct reaction of the metal with carbon.

Description of the prior art

Carbides of the metals of Groups IV–B and V–B of the Periodic Table such as titanium, zirconium, hafnium, vanadium, niobium, and tantalum are designated herein as refractory metal carbides.

Large single crystals of these refractory metal carbides would have many applications in industry. The fully dense homogeneous carbide single crystals will replace cemented and sintered carbides in many applications. For example, the carbide single crystals may be used in small diameter wire drawing dies, fine bearings for instruments and gyroscopes, high velocity hydraulic flow control devices, drills, lathe cutting tools and fiber manufacture devices such as spinnerettes. Heretofore, single crystals of metal carbide such as TiC, ZrC, HfC, VC, NbC and TaC, having high purity and homogenous composition and structure have been generally unavailable.

Although cemented carbides, hot-pressed carbides, and sintered carbides are produced commercially from powdered metal carbides they are characterized as being of a porous, or of a heterogenous structure, and are not fully dense, and they have been available only in limited shapes because they are initially produced by powder metallurgy techniques, usually employing cobalt or other metal binder and are restricted to what can be produced by grinding or etching of such compacted powder and sintered bodies.

The term "fully dense" means a carbide member which is substantially 100% of the theoretical density of the carbide based upon X-ray parameters, and is substantially free from voids or porosity. Carbides which are not fully dense, such as cemented or hot pressed carbides, have either a duplex structure of a metal and metal carbide or have up to 30% void volume present as porosity.

The best currently available metal carbide bodies are crystal boules produced by the classical techniques of controlled solidification from a melt. Modifications of the Verneuil method are used in which the end of a growing carbide crystal boule is kept molten while additional metal carbide usually powder, is sprinkled on the liquid pool. There are characteristic limitations in this technique which affect crystal quality. One limitation is the extremely high temperature required to melt the carbides since the carbides of the transition elements include some of the most refractory substances known. Controlled melting and freezing of liquids at temperatures approaching 4000° C. presents considerable difficulties. Another shortcoming of the metal carbide crystal boules is the difficulty in controlling the purity and stoichiometric homogeneity of the carbon-metal in a high temperature arc-melted or induction-melted metal carbide liquid. As a result of these limitations, the few crystal carbides currently available are characterized by strains resulting from thermally induced stresses as well as composition and purity variations. For example, it is well known that titanium carbide crystals grown by the arc-melted Verneuil method usually contain inclusions of free carbon, even when the total combined carbon-to-metal ratio is below the stoichiometric proportions for TiC.

THE PRESENT INVENTION

It has been found that high quality large crystals of a carbide of a metal from Groups IV–B and V–B, such as zirconium carbide, can be grown reproducibly and controllably under specific conditions of time and temperature by means of a direct reaction between metal and the carbon of a graphite mold containing the melted metal. These may be single crystal bodies, or if two or more large crystals are present in a body they may be readily separated in individual single crystals.

The kinetics of the direct reaction of the six elements Ti, V, Zr, Nb, Hf, and Ta with carbon has been measured over the temperature range from 1800° to 3400° C. These have been employed in the processes of this invention. The six monocarbides resulting from direct reaction are prepared in the presence of excess free carbon at a temperature from the melting point of the metal up to the monocarbide-carbon eutectic temperature. The basic process of this invention consists of (1) a multiple-step or continuously increasing temperature cycle during the phases of carbide formation and solid wall growth followed by (2) a prolonged secondary recrystallization anneal phase at a temperature close to the respective carbide-carbon eutectic temperature. The first step of the process results in the formation of an outer wall of metal carbide of progressively increasing thickness which encloses a molten pool of metal, and due to subsequent temperature increase, the molten metal pool expands and induces a plastic strain on the metal carbide wall and due to the strain at these temperatures the metal carbide texture

changes to an equiaxed, fine primary grain texture. Very large secondary recrystallization grain growth occurs thereafter on further annealing.

Accordingly, it is an object of this invention to provide methods for growing large refractory monocarbide crystals of metals.

It is another object if this invention to provide methods for growing such large metal carbide crystals reproducibly.

It is another object of this invention to provide methods of growing large refractory monocarbide crystals of transition elements by means of solid state growth techniques involving plastic strain, primary recrystallization, and secondary recrystallization grain growth of the monocarbides.

Finally it is an object of this invention to provide large crystal transition element monocarbides which accomplish the foregoing objects and desiderata in a simple and effective manner.

SUMMARY OF THE INVENTION

Generally, the present invention comprises the steps of placing a body of metal of the periodic Groups IV–B and V–B in a confining mold composed of a substantially impervious carbonaceous material, such as graphite, heating the metal and mold to a temperature above the melting point of the metal for a period of time sufficient to cause the formation of an initial metal carbide scale or shell completely enclosing the remaining unreacted liquid metal, and slowly increasing the temperature of the carbide body as it grows and has a wall of increasing thickness due to diffusion of carbon, to a temperature not exceding the metal carbide-carbon eutectic temperature, whereby the enclosed pool of liquid metal expands and exerts a plastic strain on the confining metal carbide walls, such that the final all full carbide body initially has a small equiaxed grain structure, and heating the full carbide body at a high temperature so that second recrystallization occurs by means of the plastic strain and produces a large crystal structure, the continued heating assuring a solid large crystal grain body of homogeneous composition.

For a better understanding of the invention reference is made to the drawings in which:

FIGURE 1 is a vertical sectional view through an induction heating furnace for preparing the large grain crystal carbides;

FIG. 1A is an enlarged cross-section view of a portion of FIG. 1;

FIG. 2 is a zirconium-carbon phase diagram;

FIG. 3 comprises three charts with curves showing the relationship for the same time scale, of (A) temperature, (B) average and maximum grain size, and (C) carbide wall or scale thickness, and rod diameter.

FIGS. 4 to 8 are vertical sectional views of a metal body in a mold showing the progressive changes in the metal to metal carbide transformation through various grain growth changes.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The process of the present invention involves the direct reaction under controlled time and temperature conditions of at least one of the metals of the periodic Groups IV–B and V–B, namely titanium, zirconium, hafnium, vanadium, niobium, and tantalum, or mixtures or alloys of two or more, with graphite or carbon to form a single crystal body of the metal monocarbide.

The kinetics of the direct reaction of the six metals Ti, V, Zr, Nb, Hf, and Ta with carbon have been measured over the temperature range of from 1800° to 3400° C. The full monocarbides of these six metals may be directly prepared in the presence of excess free carbon at any temperature above the melting point of the metal and up to the metal monocarbide-carbon eutectic temperature. Such eutectic temperature represents an upper limit for the growth of the monocarbides in excess free carbon. These eutectic temperatures for the several elements involved are given in Table I hereafter.

Monocarbides prepared by direct reaction in the process disclosed herein are fully dense, free of microscopic inclusions and porosity and exhibit remarkable grain boundary mobility. Suitably prolonged heating in the presence of excess free carbon results in annealed, homogeneous metal monocarbide.

In carrying out the process of this invention a suitable apparatus is shown in FIG. 1 wherein a graphite crucible **2** is provided with a plurality of charge-receiving chambers **4** which are circumferentially disposed and equally spaced within the crucible, with two chambers being visible in FIG. 1. The center of the crucible **2** is provided with a central bore **6** which serves as a pyrometer well. A graphite cover **8** is mounted on the top of the crucible **2** and a graphite tube **10** extends upwardly therethrough from the bore **6**. When assembled, the cover and crucible approximate black body conditions within the bore **6**. The crucible assembly is disposed within a silica container **12** filled with a carbonaceous material such as lampblack completely enclosing the crucible **2** and the cover **8** and allows the upper portion of the tube **10** to extend therethrough. The lampblack provides insulation and thermal stability to the system. The container **12** is mounted on a support member **14** of which the lower end is mounted on a base **16**.

The foregoing structure is disposed on a positioning rod **19** within a housing comprising a plate **18** and a silica tube **20** the upper end of which is covered with a plate **22**; a number of spaced tie bolts **24** extend between the plates **20** and **22** for holding the plates against the opposite ends of the tube **20** in an airtight manner by using annular gaskets **26** between the ends of the tube **20** and the plates **18** and **22**.

The crucible assembly is heated by an induction coil **28** of conventional construction to a high temperature to heat to melting temperature a metal charge at which temperature carbon will react with the metal to form the full carbide. An inert gas such as argon or helium is passed into the tube **20** at a pressure slightly in excess of one atmosphere. For that purpose, a gas inlet **30** communicates with a bore in rod **19** and thence to a central aperture **32** in the base **16** and in turn passes through spaced gas passages **34** in the base of the container **12**. The assembly is evacuated through an outlet **36** in the upper plate **22**. Thereafter, the inert gas is admitted and completely fills the interior of the container **12**, and the chambers **4** and as heating proceeds flushes out any remaining traces of oxygen, water vapor, or other undesirable gases. The inert gas exits through the outlet **36**. The gas outlet **36** is aligned with the tube **10** so that temperature readings may be taken with an optical pyrometer of the black body conditions within the central bore **6**.

Each chamber **4** is occupied by a mold or thimble **38**, see FIG. 1A, which is an elongated tubular member in which the metal charge **40** is inserted. One open end is closed by a plug **42**. The thimble **38** and plug **42** are composed of carbonaceous material such as graphite substantially impermeable to the liquid metal. The thimble **38** is of a sufficient outer diameter to fit snugly within the chamber **4** as shown in FIG. 1A. For some of the experiments the inside diameter of the chamber of the thimble as well as the diameter of the charge **40** varied from about 0.255 to 0.300 inch and the charge is approximately 2¼ inches long and the charge fits the thimble snugly. Although a plurality of chambers **4** are provided in the crucible **2** it is understood that the crucible could be used with only a single chamber.

After metal charges such as zirconium in the form of a solid rod placed in its thimble **38** the combined charge **40** and thimble **38** are inserted in the chambers **4** the system assembled evacuated and purged as described above

the system is heated above the melting temperature of the metal. The initial temperature in the graphite thimble **38** must be below the metal carbide-carbon eutectic temperature for the metal. Critical temperatures in the various metal-carbon systems for the indicated metals are shown in Table I as follows

TABLE I.—CRITICAL TEMPERATURES, ° CENTIGRADE

Element	Melting point	Metal carbide-carbon eutectic temperature
Titanium	1,668	2,760
Zirconium	1,857	2,890
Hafnium	2,130	3,180
Vanadium	1,710	2,760
Niobium	2,500	3,300
Tantalum	2,996	3,450

Generally, the process for ultimately growing large secondary crystals consists of heating the metal over a predetermined increasing temperature cycle beginning with an initial phase of a metal carbide scale or wall growth followed by a prolonged homogenizing anneal phase at a high temperature close to the metal carbide-carbon eutectic temperature. The process requires that during the increasing temperature cycle, while a pool of liquid metal still remains in the charge (that is before all of the metal charge **40** is consumed in carbide formation), the solid metal carbide which is formed is subjected to a plastic strain such as caused by the difference in the coefficiences of thermal expansion, as well as the volume change when the metal becomes a metal carbide, between the remaining liquid metal pool of charge **40** and the initially formed metal monocarbide shell around the liquid metal. The plastic strain so induced is critical for subsequent grain recrystallization. First, a primary recrystallization resulting in a finer equiaxed grain texture takes place at the elevated temperatures. Then secondary recrystallization takes place during subsequent annealing at the highest annealing temperatures, results in the ultimate development of a single crystal monocarbide.

The process is initiated by heating the crucible assembly of FIG. 1 up to a temperature above the melting point of the metal charge **40** which varies with the particular metal involved as indicated in Table I. At the beginning of the process the entire charge **40** is liquid as shown in FIG. 4. A direct reaction occurs between the metal charge and the carbon in the thimble whereby carbon diffuses into the charge to form a shell wall or scale of the metal monocarbide. FIGS. 4 to 8 show schematically the progressive transformation of the metal to metal carbide and the grain growth.

The heating is continued by increasing the temperature either gradually or in stepwise fashion, progressively in increments of not less than about 15° C., such as by 50° C. temperature increments, to cause the formation of a shell of equiaxed metal carbide grains. As the heating cycle continues at an increasing temperature the carbon continues to diffuse through the carbide scale **44** into the liquid metal charge **40** and forms a progressively increasing wall thickness for the metal carbide shell enclosing the liquid metal pool.

With continued increasing temperature, either gradually or by small increments, the higher coefficient of expansion of the remaining liquid metal charge **40** exerts itself radially outwardly upon the encroaching wall **44**, creating a plastic strain in the entire grain structure thereof.

A salient feature of this invention is that the temperature is increased either progressively during the formation of the metal monocarbide wall as shown in FIGS. 4 to 8, or stepwise by small increments of, say from about 25° to 100° C., each held for a period of from 2 to 12 hours, for example, depending upon the particular metal involved. Care is required that the temperature is not increased too rapidly of from about three to six steps, to avoid causing cracks due to excessive strain whereby the remaining liquid metal exudes or leaks out.

The plastic strain in the carbide shell developed under the hydrostatic pressure of the expanding liquid metal is an initiating force in primary recrystallization of the carbide. That is, the atoms of the solid are rearranged into a new set of crystallites which are very small and of relatively great crystalline perfection (FIG. 6).

With continued heating at increasing temperatures the diffusion of carbon into the remaining metal charge 40 is completed so that the thimble **38** is eventually wholly occupied by a single monocarbide body **46** (FIG. 7) composed of many grains. After some of the metal is converted to the metal carbide, and primary recrystallization has been effected heating at the highest temperatures is continued so that the carbide enters an exaggerated grain growth or secondary recrystallization phase (FIG. 7), whereby one or a few grains grow at the expense of the surrounding primary grains. The growth continues with continued annealing below the monocarbide-carbon eutectic temperature until one or a few large crystals **48** occupy the entire body of the carbide member, as shown in FIG. 8.

The multiple step, increasing temperature cycle has been successfully practiced with six to eight steps or incremental temperature increases. The process has been practiced with a one step increase but the secondary grain growth is not as complete as that when a multiple step process is followed. Other temperature increase modifications have also been found to produce large secondary metal carbide crystals. The stepwise increase in temperature may be replaced by a slow continuously increasing temperature rise during the same phase in growth of the metal carbide.

The mechanism postulated for large secondary crystal growth is based on a sequence of plastic strain, primary recrystallization, and secondary recrystallization. Although it is developed at high temperatures, the plastic strain is equivalent to cold work in conventional metals. The carbide grains store strain energy during deformation in the form of an increased dislocation density. During subsequent annealing the dislocations organize into polygonal networks which become the new grain boundaries for the recrystallized material. Thus the primary recrystallization involves a marked reduction in grain size. Once the carbide has undergone primary recrystallization, it is essentially strain free and has a low dislocation density relative to the unstrained starting material. However, it is believed that some of the strain energy stored during deformation remains in the primary recrystallized material as the increased surface energy of the refined grain structure. Reduction of this surface energy is the driving force for secondary recrystallization, which is the process of growth of the new grains.

The movements of dislocations leading to primary recrystallization and the movements of grain boundaries during secondary recrystallization both tend to clear the bulk of the material of line defects. Therefore, crystals of relatively high physical perfection, with low residual strains and low dislocation densities, are possible.

The following example illustrates the practice of the invention:

EXAMPLE

Six specimens of high purity zirconium rods were prepared with a nominal diameter of 0.25 inch and a length of from 2.25 to 2.50 inches. After cutting to dimension the zirconium rods were surface cleaned in an etchant composed of 50 parts H_2O, 50 parts HNO_3 (concentrated) and 15 parts HF (50%). The etchant removed 0.010 inch of diameter from the zirconium rod in about 10 seconds. Thereafter, the rods were placed in the thimbles or molds **38** and the caps **42** for placement in the crucible **4** of the furnace of FIG. 1.

After evacuation and purging with argon gas, the furnace was heated to a temperature of 2200° C., above the melting point of zirconium. The phase diaphragm for

irconium is shown in FIG. 2. For zirconium the preferred starting temperature is about 400° C. above the melting point of zirconium; accordingly the starting temperature of the process was approximately 2200° C. The samples were heated for periods of 12 hours at this temperature, then raised 50° C. and held for another 12 hours, and 50° C. temperature increments were applied for periods of 12 hours until 2500° C. was attained and held, and then increased to 2700° C. and held for 64 hours. When cooled to room temperature, the rods were all high density full zirconium carbides composed of large secondary recrystallized grains. Some rods had only one or two grains, others had several grains. Sometimes a small island of a few small grains was present, usually at the rod ends. These could be readily removed. Rods could be severed at the grain boundaries to produce large single crystals.

By practicing the process of Example I, using however an initial temperature equal to the melting temperature of the metal plus from 10° C. to as much as 400° C. to 500° C. (the former for vanadium), but otherwise following the temperature and time increments, we have obtained large secondary grain texture carbides of these metals, for example, HfC, TiC, ZrC and VC. The hafnium metal containing 3% Zr by weight, and formed excellent large secondary grains. In all cases the large refractory metal carbide crystals are far superiod crystallographically and chemically to the Verneuil boule products.

A series of experiments were conducted. After establishing equilibrium in the furnace zirconium specimens were each heated at temperature increments of 50° for the time periods shown in Table II and withdrawn for inspection.

TABLE II.—THERMAL HISTORY OF SEQUENTIAL CRYSTAL GROWTH SAMPLES

Sample No.	Sequence of temperature (° C.) holds	Time at each temp., hrs.
1	2,200 (blank)	0
2	2,200	12
3	2,200, 2,250	12
4	2,200, 2,250, 2,300	12
5	2,200, 2,250, 2,300, 2,350	12
6	2,200, 2,250, 2,300, 2,350, 2,400	12
7	2,200, 2,250, 2,300, 2,350, 2,400, 2,450	12
8	2,200, 2,250, 2,300, 2,350, 2,400, 2,450, 2,500	12
35	2,200, 2,250, 2,300, 2,350, 2,400, 2,450, 2,500	12
	Plus 2,700	64

The consecutive Samples 1 to 8, and 35 removed for study and the results are shown in FIG. 3 of the drawings in which the grain size, and carbide wall thickness as well as rod diameter are correlated with the time-temperature increments.

As shown in chart (B) the initial carbide grain growth period (A) dominates the first four temperature increments up to a temperature of approximately 2350° C. over a period of about 48 hours. With increasing temperatures the equiaxed grains developed during the first period (A) were subjected to plastic strain by the liquid metal, thereafter the primary recrystallization phase occurs during period (B) whereby the grain size of the carbide becomes exceedingly small as the temperature increases from about 2350° C. to about 2450° C. In period (C) with increasing temperature one or more of the small grains grows at the expense of adjacent surrounding grains whereby the secondary recrystallization phase occurs with the resulting monocarbide body being entirely dominated by one or a few large crystals. As shown in the lower portion of FIG. 3C, the scale thickness and rod diameter increase as the carbide is formed. The specimens having an original diameter of 0.27 inch were found to have increased to a final diameter of 0.30 inch.

During the final stages of the heating process the carbide body **48** becomes completely carburized and the gradient of high carbon at the periphery and low carbon at the center of the body is eliminated so that the zirconium carbide specimens have about 49.5 atom percent carbon across their entire cross-section after the final heat treatment.

The solubility rates of carbon in liquid zirconium and initial grain growth are so fast that a scale or shell of a few thousandths of an inch thick built up on Sample No. 1 (Table II). This sample was at temperatures above the melting point for no more than a few minutes, yet there was a pick up of 2.03 weight percent carbon which agreed with the measured recession of the graphite thimble wall. The carbon in zirconium in excess of the solubility precipitated at the graphite-liquid metal interface in the form of a thin (0.002 to 0.003 inch) carbide scale. The dimensions of the grains in the scale were on the same order as its thickness. The scale in Sample No. 1, like the scales or shells through Sample No. 5, was strongly adherent to the graphite thimble surface.

Samples No. 2 through No. 5 showed steady increases in rod diameter, scale or shell thickness, and grain size over the conditions of Sample No. 1. The grains remained equiaxed and none displayed exaggerated grain growth. The grain size of Sample No. 6 however decreased abruptly in size to an average of 0.005 inch. When this grain refinement occurred, the rod diameter had nearly reached its final value of 0.300 inch and the metal carbide wall had grown a little more than halfway to the rod axis. This sample did not adhere to the thimble wall. Sample No. 7 was essentially the same as Sample No. 6 except for a slight (about 0.005 inch) increase in rod diameter.

Sample No. 8 definitely exhibited initial exaggerated or secondary grain growth; that is, a few grains had elongated rapidly while the majority of the grains remained small. After the final high temperature anneal only a few large grains remained in the entire sample. This was confirmed by the sharpness of a Laue X-ray pattern taken from a random sampling across the rod's cross section. The lattice parameter of the material was 4.6997A which corresponds to about 49.5 atom percent C. The weight increase in the zirconium sample due to carbon pickup was 13%. This is equivalent to 11.5 weight percent C in the resulting ZrC.

The foregoing observations confirm our understanding of the proposed crystal growth mechanism. The diameter increases of Samples Nos. 1–6 are evidence of plastic strain. The grain refinement exhibited in Sample Nos. 6 and 7 is exemplary of primary recrystallization. The subsequent rapid growth of a few grains in Sample No. 8 exemplifies secondary recrystallization, and a few large grains comprising the whole of Sample No. 35 completes the secondary recrystallization growth pattern. Other samples were subjected to the entire heating program without interruption and reproduced the large grains of single crystal quality.

The concept and techniques described have also been successfully applied to producing metal carbides of the Groups IV–B and V–B metals. Six large crystals of approximately one inch long can be prepared reproducibly from a run containing six 2 inch zirconium rods. These crystals have the full rod diameter and have been grown with diameters ranging from about 0.187 to 0.30 inch. However larger rods or bodies can be readily prepared.

Although process variations in materials, gradients, seeding, surface preparation etc. have been tried, abnormally large secondary grains have only been grown by following the critical variations in the time and temperature in the carbide growth and recrystallization phases of the process herein disclosed.

It is essential to use increasing temperatures during growth of the carbide and recrystallization. Thus, many attempts to grow ZrC rods at a single temperature throughout the complete process failed to produce abnormally large grains. However, equiaxed, small grains resulted from isothermal, direct reaction of zirconium with carbon at temperatures from 2200° to 2700° C. The smallest grain sizes of ZrC were grown at the lowest isothermal annealing temperatures.

It is understood that the above specification and drawings are exemplary of technically and economically feasible methods of producing large single crystals of carbides of the metals of periodic groups IV–A and V–A.

What is claimed is:

1. A method of producing a body having at least one large secondary crystal of refractory metal carbide comprising enclosing with a carbonaceous material a body of at least one metal of the group consisting of Ti, Zr, Hf, V, Nb and Ta and alloys of two or more thereof, heating the enclosed body while in contact with the carbonaceous material to a temperature in the range above the melting point of the metal body and below the metal carbide-carbon eutectic temperature, the heating causing progressive formation of a metal carbide shell beginning with the liquid metal interface with the carbonaceous material, the temperature being increased as the metal carbide shell increases in thickness until all the liquid metal is converted to metal carbide so as to impose a plastic strain on the metal carbide, the resulting metal carbide being annealed at an elevated temperature below the metal carbide-carbon eutectic temperature whereby in combination with the plastic strain, primary recrystallization takes place, and continuing the heating at the elevated temperature until secondary recrystallization of the metal carbide occurs to produce large secondary crystals of the metal carbide.

2. The method of claim 1 in which the body is heated to progressively higher temperatures.

3. The method of claim 1 in which the body is heated progressively at increased increments at periodic intervals.

4. The method of claim 1 in which the body is heated in multiple increments of increasing temperature.

5. The method of claim 4 in which the temperature is increased in from about three to six steps of increased temperature.

6. The method of claim 4 in which the temperature is progressively increased at increments of not less than about fifteen degrees centigrade.

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