

[54] REFRACTORY COMPOSITE ALLOYS
CONTAINING ROD-LIKE AND/OR
PLATELET-LIKE LAMELLAE

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[63] Continuation-in-part of Ser. No. 2,160, Jan. 12, 1970, abandoned.

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Dec. 23, 1969 France 69.44708

[52] U.S. Cl. **29/191.2**, 75/170
[51] Int. Cl. **B32g 15/00**, C22c 19/00
[58] Field of Search 75/170

[56]

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3,124,452	3/1964	Kraft.....	75/135
3,157,495	11/1964	Eiselstein et al.....	75/170 X
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3,340,077	9/1967	Alper et al.....	75/170 X
3,528,808	9/1970	Lempkey et al.....	75/170
3,564,940	2/1971	Thompson et al.....	75/170 X

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[57]

ABSTRACT

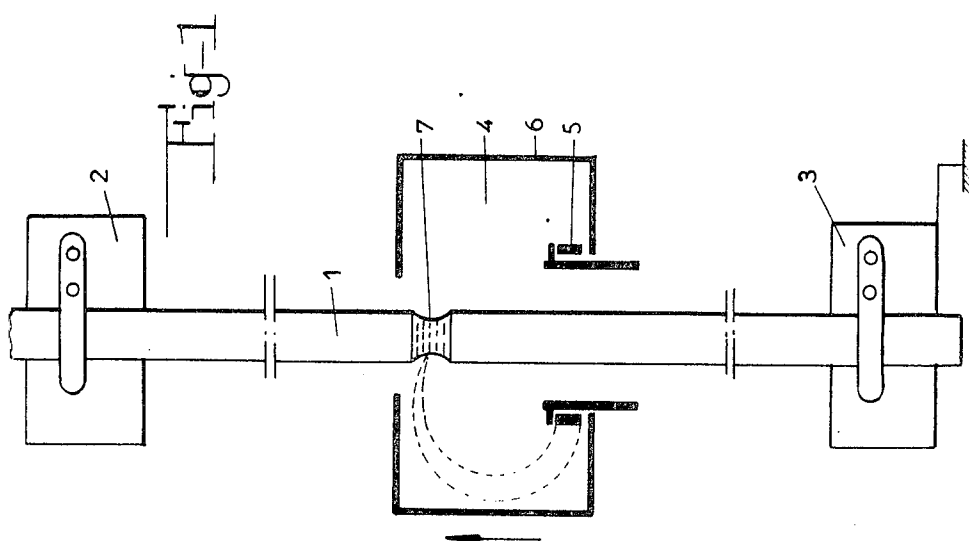
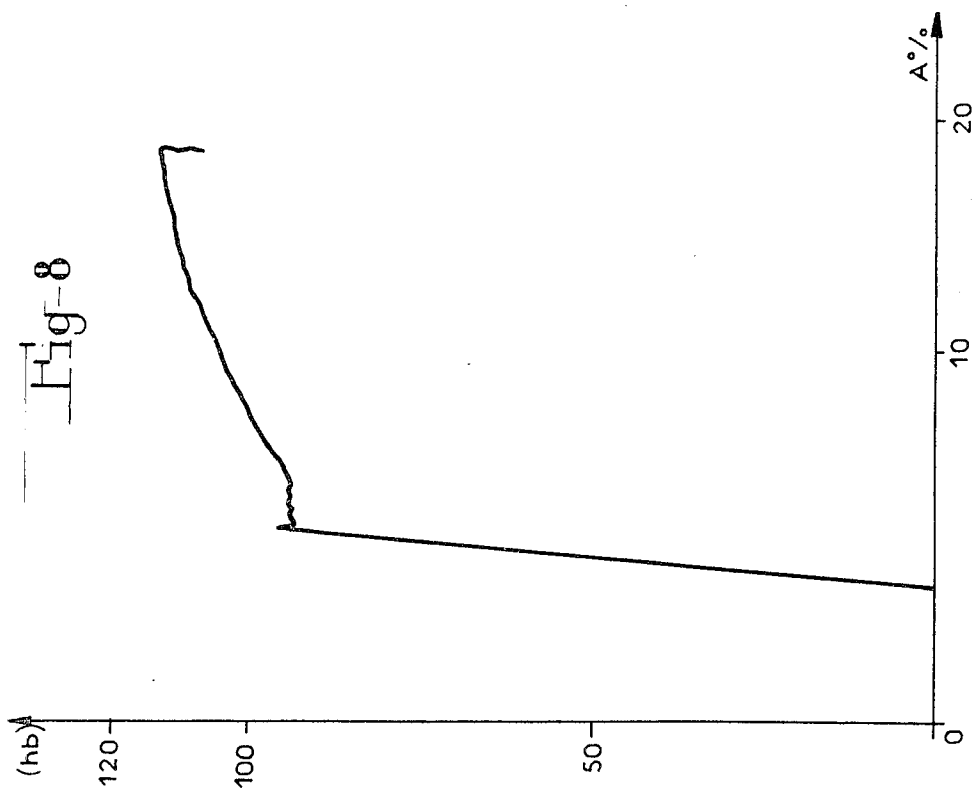
Polyvariant alloys which comprise a matrix and a directional reinforcement phase imbedded in said matrix in form of chromium-free mono-crystalline particles of carbide. The method for the manufacture of such alloys involves zoning a rod under determined conditions of movement rate and thermal gradient at the solidification interface of the rod.

16 Claims, 19 Drawing Figures

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SHEET 01 OF 10



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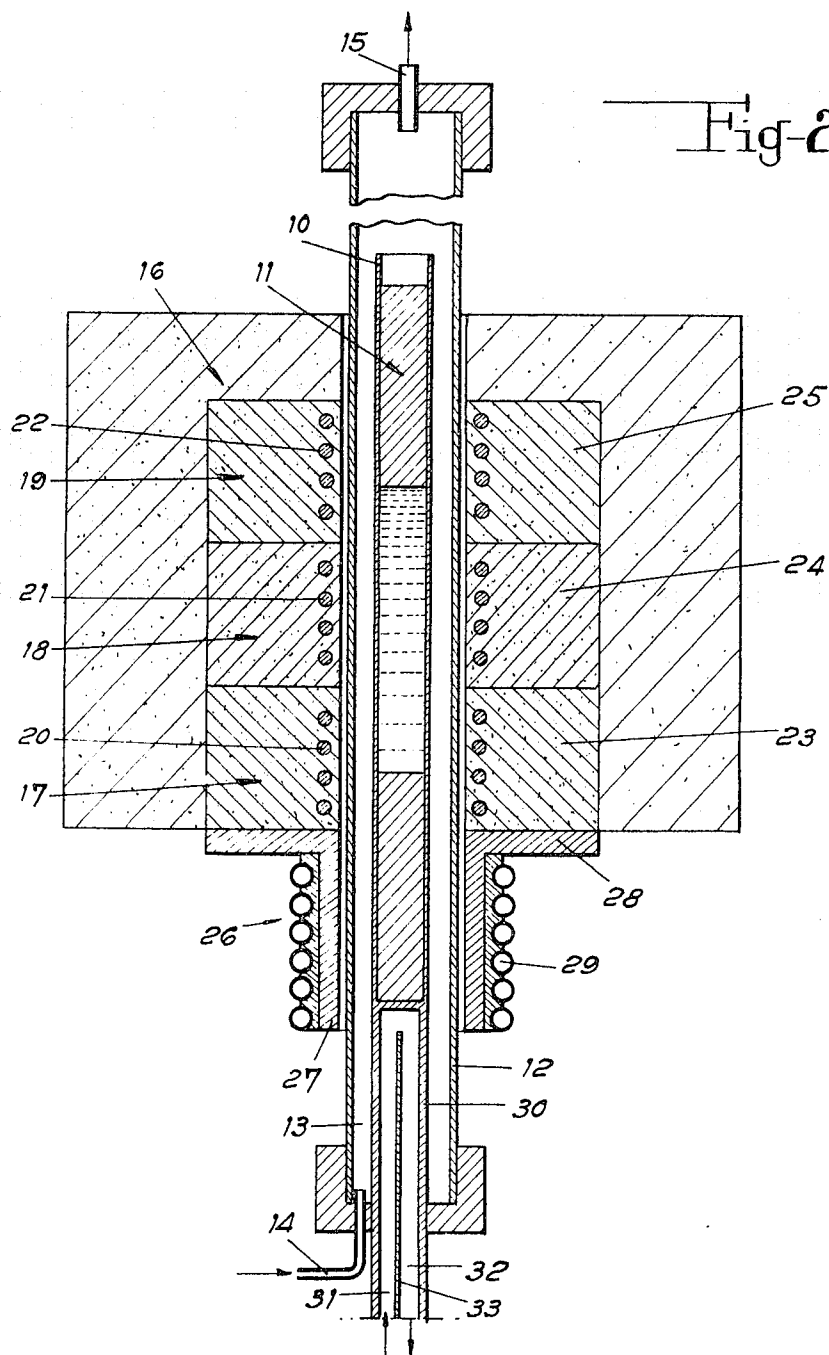


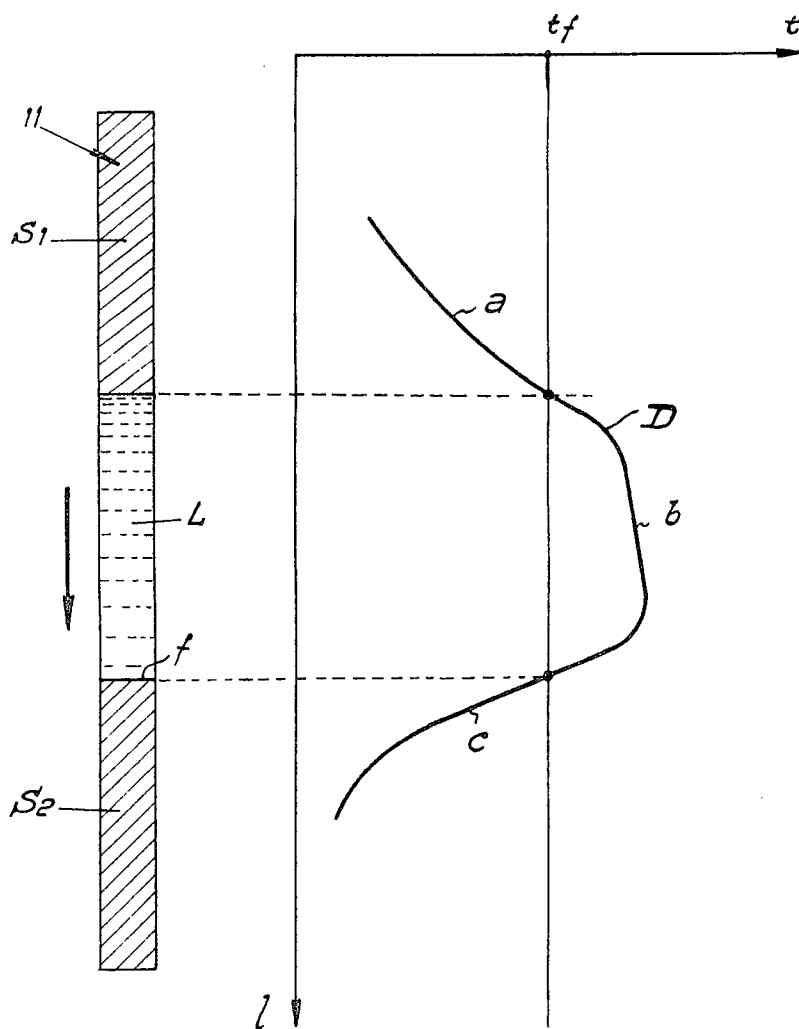
Fig-2

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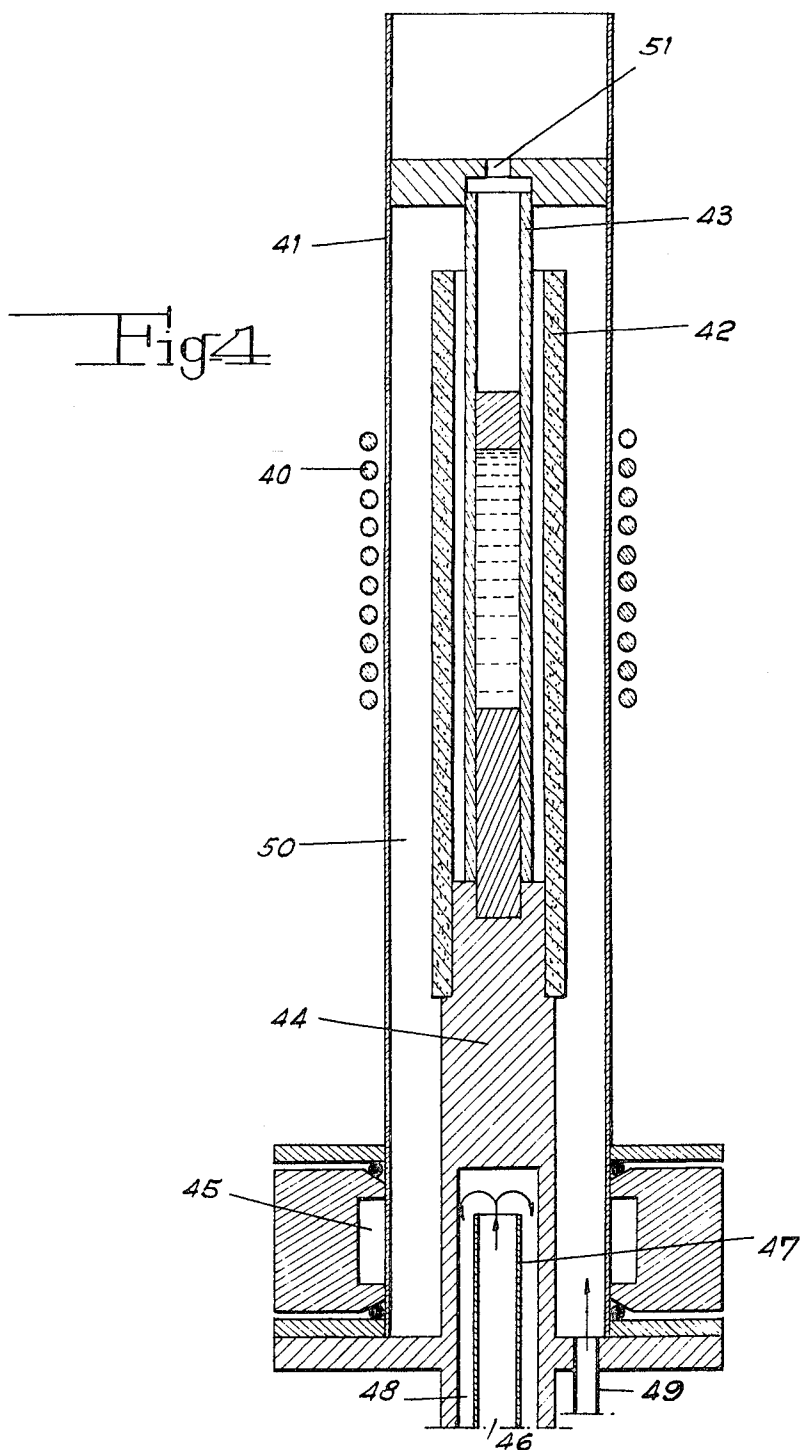
Fig-3



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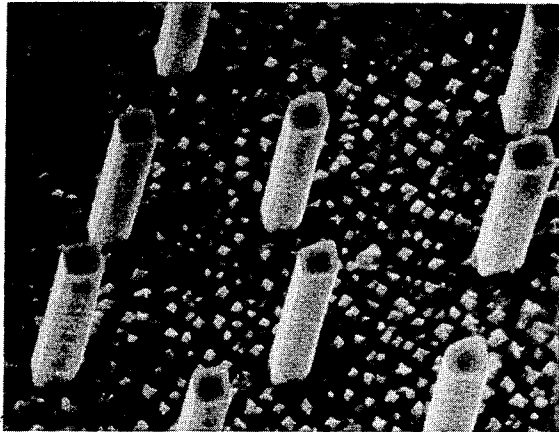


FIG. 5



FIG. 6

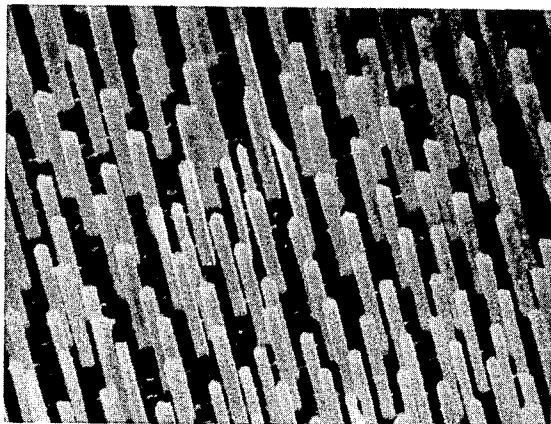


FIG. 7

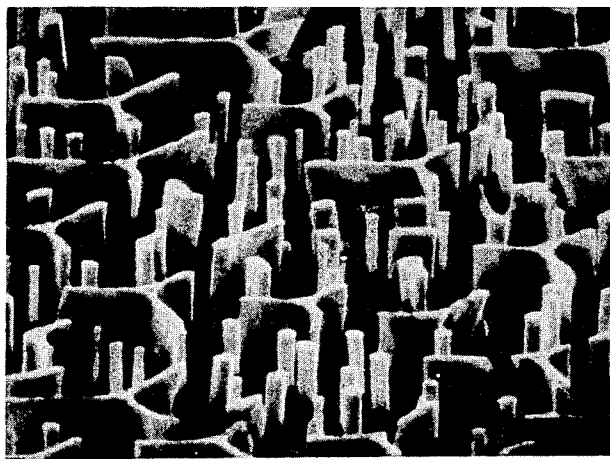


FIG. 9a

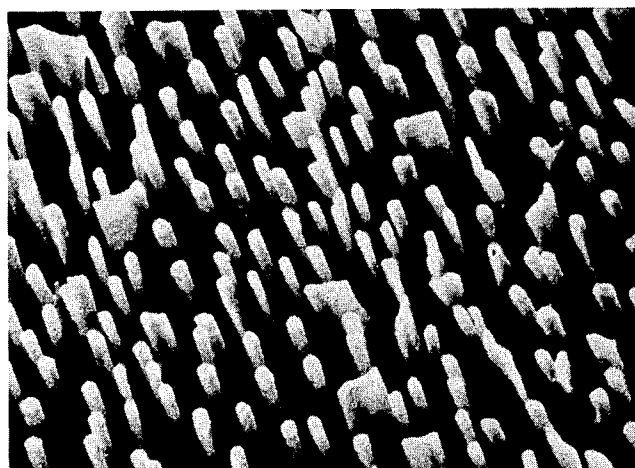


FIG. 9b

FIG.10

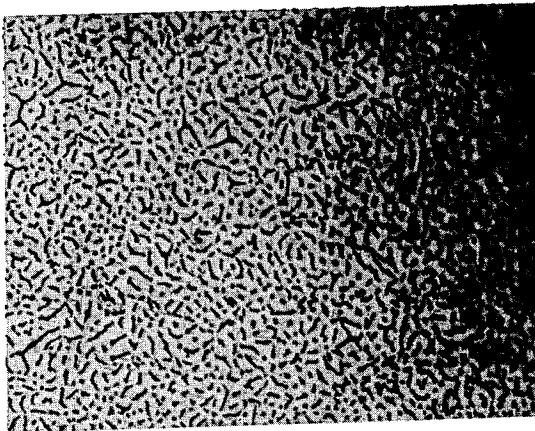
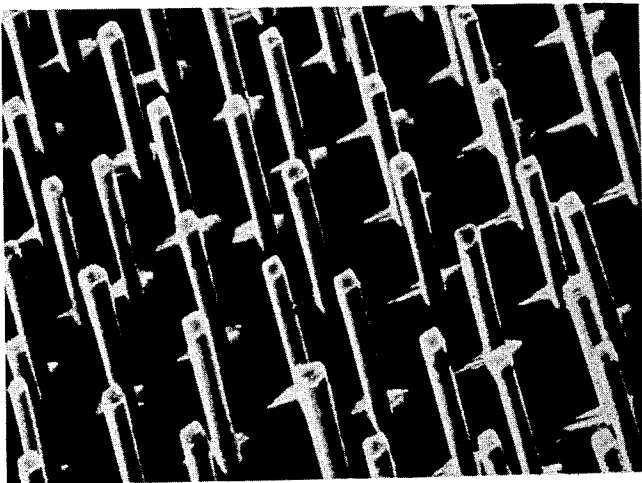


FIG.11



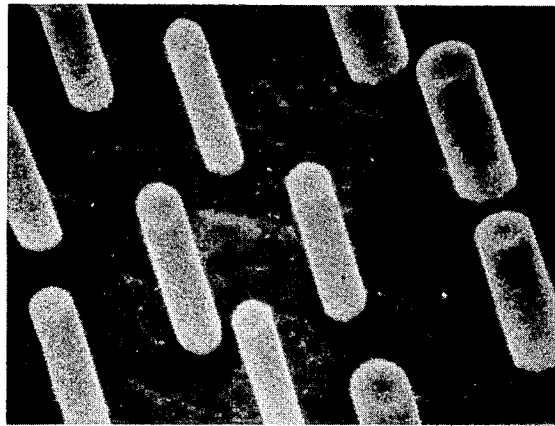


FIG. 12

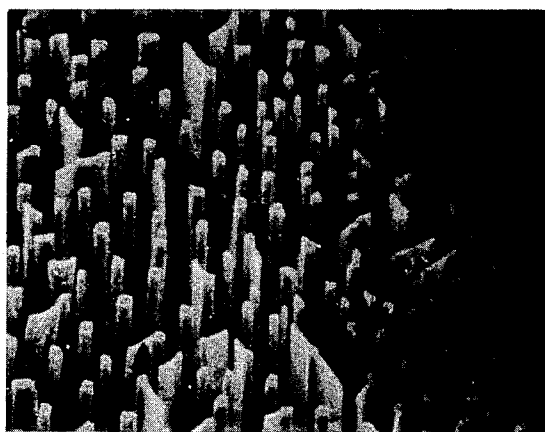
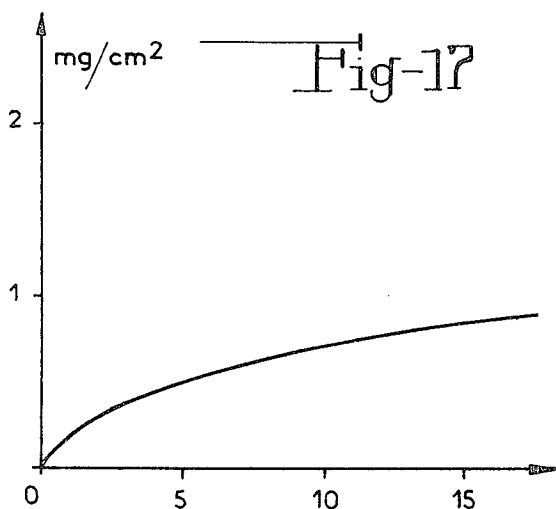
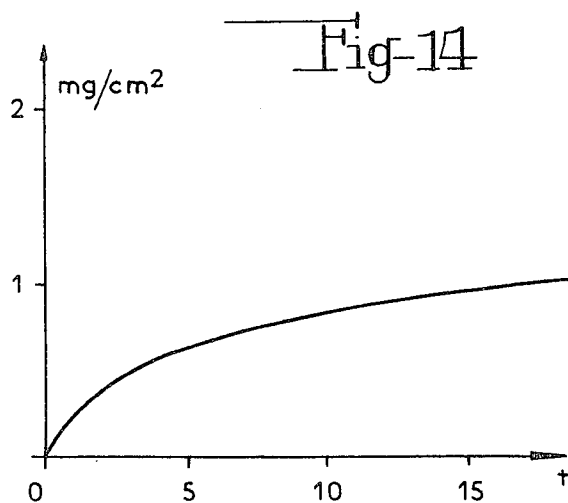


FIG. 13



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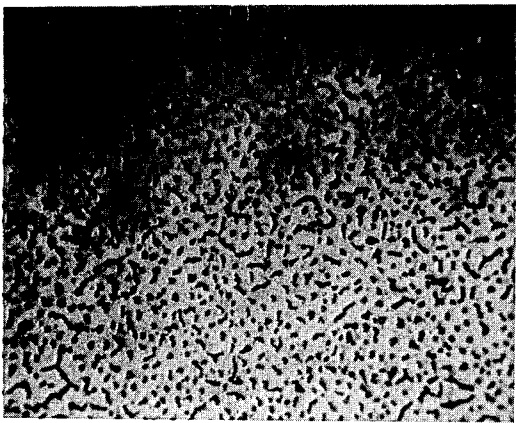


FIG. 15

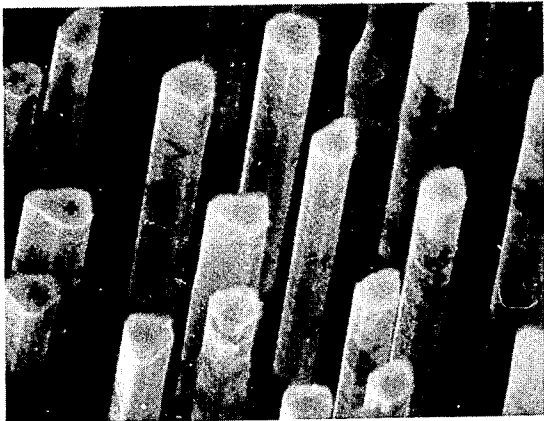


FIG. 16

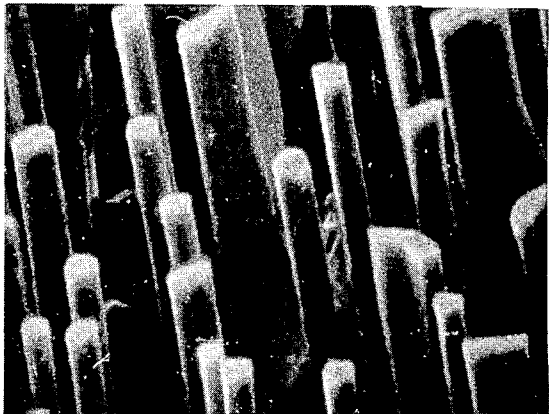


FIG. 18

REFRACTORY COMPOSITE ALLOYS CONTAINING ROD-LIKE AND/OR PLATELET-LIKE LAMELLAE

CROSS-REFERENCE TO COPENDING APPLICATION

The present application is a continuation-in-part of our copending application Ser. No. 2,160 filed Jan. 12, 1970 (now abandoned).

FIELD OF THE INVENTION

The present invention relates to refractory composite alloys containing single crystalline rod-like and/or platelet-like lamellae, their manufacturing method, as well as an apparatus for carrying into effect said method.

BACKGROUND OF THE INVENTION

The manufacturing of metallic composite compounds, containing rod-like and/or platelet-like lamellae, by unidirectional solidification of eutectic binary alloys has already been proposed, as for example in the KRAFT U.S. Pat. No. 3,124,452.

However, since the metallic matrix of a binary alloy is unable to offer a sufficient resistance to high-temperature corrosion, only compounds having unsatisfactory properties and especially the inability to resist high-temperature corrosion have been prepared by such a method.

It has also been proposed to provide alloys with a ternary eutectic composition having two phases, one a matrix either of nickel, cobalt or chromium, the other a reinforcement phase which is oriented and in the form of fibers (fibrous phase) contributing high corrosion resistance at elevated temperatures. The fibrous phase is composed of a monocarbide of a transition metal (i.e., titanium, zirconium, hafnium, vanadium, niobium or tantalum — see U.S. Pat. No. 3,528,808).

There have also been suggested alloys consisting of a monovariant ternary eutectic with a matrix of an alloy of nickel or cobalt and a fibrous phase (phase of a whisker or lamellar morphology in substantial alignment) constituted of a carbide or mixture of carbides of transition metals (i.e., the carbides of niobium, tantalum, titanium, vanadium, zirconium, hafnium, chromium and cobalt); another prior-art alloy of the ternary type includes the system in which nickel aluminide forms the matrix and contains fibers of chromium (see U.S. Pat. No. 3,564,940).

As has been pointed out in the literature, all of these alloys or systems are of substantially monovariant composition, i.e., the difference between the number of elements contained in the alloy and the number of phases is at most unity. This has posed severe restrictions upon prior-art attempts to extend the principles described above to more complex systems and thereby to further improve the properties of metal-matrix/metal-carbide fiber systems. While we do not wish to be bound to any theory as to why the prior-art systems have been limited to monovariance, as noted above, and have hitherto failed to comprehend a variance of two or three or more (i.e., systems in which the difference between the number of metallic elements present and the number of phases is two, three or more), the reasons are probably the following:

— the phase diagrams of quaternary, quinary or of higher-order systems are not well known;

— the necessity of taking into account the partition coefficients — i.e., the ratio, at a given temperature, of the concentration of an element in the solid phase to its concentration in the liquid phase — of all the present elements excessively complicates the establishment of the solidification conditions to be used; and

— in order to prepare materials are to be used at very high temperatures, melting and solidification must be achieved at very high temperatures, so that the operating conditions which must be used in the unidirectional solidification process become exceedingly difficult to maintain.

The difficulties encountered with the aforementioned prior-art systems are the following:

Alloys having a matrix based upon cobalt, nickel or iron manifest poor resistance to corrosion at high temperatures, especially when they do not contain a significant proportion of chromium. In such systems, the limitation to monovariance or, as noted, the limitation upon the number of chemical elements present because the final structure is obtained by directional solidification has the following consequences:

Where it is not possible to introduce chromium in sufficient proportions into the matrix, the resistance of the alloy to high-temperature corrosion is poor.

Where chromium is introduced into the matrix at higher levels, it is also found to be present in the reinforcement phase in the form of the carbide Cr_3C_7 . As pointed out by J. R. LANE and N. J. GRANT (*Transactions of the A.S.M.*, XLIV, 1952, pp 113 – 137: Carbide Reactions in High Temperature Alloys), at temperatures between 730° and 870° C, the latter carbide tends to be transformed into Cr_{23}C_6 with liberation of carbon which is retained in the matrix in the form, for example, of Cr_{23}C_6 . As a consequence, a finely divided disperse phase is created. In effect, the fibrous phase of a reinforcement alloy provides strength-increasing fibers with a contribution to the tensile strength which depends upon the continuity and homogeneity of the fibers, the latter being bonded together by the matrix. With carbon-loss transformation described above, both of these critical characteristics of the fibrous phase, as well as the vital bond between the matrix and fibers, are adversely affected, the fibrous phase being replaced by a dispersed phase.

If one attempts to avoid this difficulty by increasing the chromium content of the reinforcement phase, the partition function comes into play to simultaneously increase the chromium content of the matrix phase.

Since it is almost impossible to exclude trace elements, such as nitrogen, which render chromium alloys fragile when they include solid solutions rich in chromium, this approach has been self-defeating.

OBJECTS OF THE INVENTION

One of the main objects of the present invention is that of providing a new metallic composite product which is composed of at least four chemical elements, containing rod-like and/or platelet-like lamellae imbedded in a metallic matrix, prepared by unidirectional solidification and which evidences good mechanical properties (especially flow stress) at room temperature as well as at high temperatures.

One of the more particular objects of our present invention resides in providing such a composite metallic

compound which can stand dry corrosion at temperatures of about 1,000° C, and which consequently is of considerable technical interest.

Another object of our present invention is to provide ductile alloys which can be used in making pieces having significant deformation capacity before breaking.

Another object of our invention is to provide alloys showing a high resistance to thermal strain, i.e., to repeated temperature variations.

Another object of our invention is to provide such alloys exhibiting a high yield point at high temperatures as well as at room temperature.

One of the principal objects of the present invention is, therefore, to provide alloy systems with a reinforcement phase by directional solidification in which the degree of variance can exceed unity, thereby permitting optimization of both the matrix and reinforcement-phase elemental compositions.

Still another highly important object of the invention is to provide alloys with high resistance to corrosion at high temperatures and yet free from the increased fragility which has characterized the alloys produced in earlier attempts to provide reinforcement-phase systems.

A crucial object of the invention is to provide an improved alloy with resistance to corrosion at elevated temperatures which possesses a reinforcement phase which is absolutely stable at all temperatures up to the temperatures of use.

It is also an important object of the invention to provide an oriented alloy comprising two or more reinforcement phases, and a process for making the alloy, in which one phase is an aligned fibrous reinforcement phase in the matrix and the other reinforcement phase is dispersed in the matrix and serves to increase the resistance of the alloy to shear and the alloy hardness.

Another object of the invention is to provide an iron-based, cobalt-based or nickel-based matrix in an alloy which, in addition, comprises chromium and another metallic element such that the oriented (fibrous) reinforcement phase consists entirely of carbides of this other element and is entirely free of chromium, i.e., there is no chromium carbide in or as the fibrous oriented reinforcement phase.

SUMMARY OF THE INVENTION

The invention is based on our finding of the existence, in the ternary Co—Ta—C system, of a eutectic point in a pseudo-binary diagram in which one of the phases is tantalum carbide, TaC, cobalt being the other phase. The pseudo-binary eutectic point, evidenced by thermal analysis, corresponds to a composition of approximately 13 percent by weight of TaC and to a temperature of about 1,400° C; it is then possible to prepare compounds having excellent mechanical properties, by unidirectional solidification.

The invention is also based on the observation that the Co—Cr phase diagram has a very flat shape for chromium concentrations up to 25 percent, and the application of our method to the complex system Co—Cr—Ta—C leads during the progressive solidification to a crystallization of carbide TaC in a cobalt-chromium solid-solution matrix. We have thus prepared a new composite metallic compound containing rod-like and/or plateletlike lamellae of TaC in a chromium-containing matrix, which provides oxidation resistance at high temperatures.

In its most general sense, therefore, the invention comprises an alloy with plural variance consisting of a matrix and a fibrous, oriented reinforcement phase wherein the matrix is essentially composed of chromium and at least one other metal selected from Group VIII of the 4th Period of the Mendeleev Chart of the elements, namely iron, cobalt or nickel, and the reinforcement phases consists essentially of monocrystalline particles of a carbide of a metallic component substantially free from chromium and including at least one metal selected from Groups IVb and Vb of the Mendeleev Chart.

The invention thus comprises the remelting-/resolidification treatment of a bar of an alloy of at least one metal of Group VIII of Period 4 of the Mendeleev Chart of the elements, of chromium, of carbon and of at least one of the transition metals of Groups IVb and Vb of the Mendeleev Chart, the transition metal and carbon being present in the alloy in stoichiometric proportions, under conditions which form a reinforcement phase (directed solidification). The treatment, where the chromium content does not exceed 25 percent by weight, yields a matrix consisting of a solid solution of chromium in the metal of Group VIII, Period 4, and an oriented reinforcement phase constituted by monocrystalline elongated particles of one or more carbides of the metals of Groups IVb and Vb. Thus the chromium is practically totally in solid solution in the metal or metals of the matrix and the metal or metals of Groups IVb and Vb are practically totally in combination with carbon in the reinforcement phase. There is, therefore, no chromium (Group VIb) in the latter phase to adversely affect the properties of the alloy.

Our method makes also possible the preparation by unidirectional solidification of new composite metallic compounds in which the cobalt part is completely or partially played by nickel or iron, the invention making use of the fact that the Ni—Cr and Fe—Cr phase diagrams have also a very flat shape up to a relatively high ponderal composition of chromium, of about 45 percent for the nickel-chromium diagram.

The new composite metallic compounds embodying our invention contain then rod-like or platelet-like TaC lamellae in a Ni—Cr matrix, or in a Co—Ni—Cr matrix, or also in an Fe—Ni—Cr matrix.

According to another feature of our invention, the matrix is advantageously formed by an austenitic solid solution, e.g. one based on iron and/or nickel and/or cobalt, which crystallizes in the face-centered-cubic lattice.

Such a matrix does not show any allotropic transformation from room temperature to the melting point, and thus offers the advantage, among others, of not exhibiting any brutal dimensional variations, on temperature changes, which could cause, for instance, more or less localized deformation, or internal stresses.

According to one embodiment of the present invention, the matrix is made of an Ni—Cr—Al alloy hardenable by precipitation.

The tantalum and hafnium carbides being miscible in any proportions, the application of our method to complex starting systems, including both tantalum and hafnium, leads too new composite metallic compounds in which the rod-like and/or platelet-like lamellae imbedded in the matrix are made of a solid solution of tantalum carbide, TaC, and hafnium carbide, HfC.

In many cases, tantalum can be replaced by other metals, especially transition metals of the IVb of the Mendeleiev Chart, i.e., titanium and zirconium, as well as transition metals of the Vb period, i.e., vanadium, niobium and hafnium.

According to another feature of our invention, the metal or metals of the carbides of the unidirectional solidification or reinforcement phase are incorporated in excess in the alloy so that one part of this metal or these metals forms with the constituent elements of the matrix, either a solid solution or one or more intermetallic compounds which increase the mechanical properties of said matrix, that part acting as an additional element for the matrix.

According to one preferred embodiment, titanium is the metal forming the carbide of the reinforcement phase.

The expansion coefficient of titanium carbide is, indeed, very close to that of the nickel-based and/or cobalt-based matrices; this avoids, on temperature variations, the development of any stresses along the matrix reinforcement-phase interfaces.

Nonrestrictive examples of complex starting systems, leading to alloys according to our invention are cited hereunder:

Co - Cr - Ta - C	Fe - Ni - Cr - Ta - C
Co - Cr - Nb - C	Ni - Cr - Ta - C
Co - Cr - Ta - Hf - C	Ni - Cr - Nb - C
Co - Ni - Cr - Ta - C	Ni - Cr - Al - Ta - C
Co - Ni - Cr - Nb - C	Ni - Cr - Al - Ti - C
Co - Ni - Cr - Ta - Hf - C	

The alloys according to our invention are made by progressive unidirectional solidification in an apparatus which permits establishment of predetermined values of the operating parameters, such as the temperature of the liquefied zone of a previously prepared rod, and of the resolidified zone, the movement rate of a solidification interface, the flat shape of a solidification interface, the temperature gradients across said solidification interface etc.

Where the metallic component of the reinforcement phase (carbide-forming elements) are tantalum, titanium or niobium as noted above, these elements are present in the alloy in amounts of substantially 10 to 18 percent by weight, 8 to 12 percent by weight and 7 to 17 percent by weight, respectively. The chromium content of the alloy is preferably 5 to 25 percent by weight and the matrix phase is preferably an austenitic solid solution. Furthermore, when aluminum is present as an additional metal other than the metals of Group VIII, Period 4 of the Mendeleiev Chart and other than the metallic component of the carbide reinforcement phase, it is present preferably as an intermetallic compound with one of the other matrix-phase elements in an amount of substantially 2 to 6 percent of the alloy. In another preferred embodiment of the invention the reinforcement phase is a single-phase solid solution of substantially 80 percent by weight tantalum carbide and 20 percent by weight hafnium carbide. The elongated monocrystalline particles of the reinforcement phase preferably have a smallest transverse dimension of substantially 0.3 to 2 microns and a length at least equal to 3,000 times their smallest transverse dimension.

In other general terms, the invention also comprises an alloy of a chromium-containing solid solution matrix

and, imbedded in this matrix, a directional (elongated) reinforcement phase in the form of monocrystalline particles (preferably extending parallel to each other) and a reinforcement phase in the form of substantially point-like particles dispersed in the matrix. As a divariant or polyvariant system the alloy can be considered to comprise at least four chemical elements forming a metallic matrix (preferably containing chromium in solid solution) and a directional reinforcement phase (chromium-free) in the form of elongated monocrystalline particles.

6. DESCRIPTION OF THE DRAWING

Other features and advantages of our invention will be clear from the following description given with reference to the accompanying drawing in which:

FIG. 1 is a schematic view of an embodiment of an apparatus used in making alloys of the present invention;

FIG. 2 is a schematic view of a modified apparatus; FIG. 3 is a diagram showing the temperature variation along a rod;

FIG. 4 is a schematic illustration of another type of apparatus used in making alloys of the present invention;

FIGS. 5, 6 and 7 are photomicrographs of alloys of the present invention;

FIG. 8 is a diagram;

FIG. 9a, 9b, 10 - 13 are photomicrographs of alloys of the present invention;

FIG. 14 is a diagram;

FIGS. 15 and 16 are photomicrographs of alloys of the invention;

FIG. 17 is a diagram; and

FIG. 18 is a photomicrograph of an alloy according to the invention.

SPECIFIC DESCRIPTION

Reference is first made to FIG. 1 which shows schematically an apparatus used in making the compositions according to the present invention and which is of the electron-bombardment floating-zone type.

The rod 1 of the alloy to be treated is set up in vertical position, in a vacuum chamber (not shown) by clamping its two ends in locking means 2 and 3, the latter being grounded. An annular electron gun 4 surrounds concentrically the rod 1 and can be moved at constant rate in a vertical translation motion by means of a screw-and-nut drive mechanism (not shown).

The electron gun comprises a tantalum filament 5 heated to high temperature by Joule effect and emitting electrons. The filament has a high negative voltage with respect to the grounded rod 1 which is to be treated. In order to focus the electrons which are bombarding the rod along and annular zone, a tantalum chamber 6 placed around the filament and rod has the same negative voltage as the filament. This arrangement, in which filament and melted zone 7 are not in a direct line of sight of each other, avoids any reciprocal contamination by the metallic vapors which both emit. The necessary thermal gradient is established by cooling the solidified zone by radiation.

At the beginning of the run, the mounting of gun 4 is placed at the lower part of the rod; the rate of upward motion can range from 0.5 to 30 cm/hour.

In FIG. 2 there is shown another apparatus used in producing the alloys according to our invention. The

apparatus comprises a fixed refractory tube 10 inside which a metallic rod 11 is placed, the composition of the rod corresponding to that of the desired alloy. The tube 10 is surrounded by another fixed tube 12 of larger diameter, the space 13 between the two tubes being filled with a protective gas circulating from an inlet pipe 15 to an outlet pipe 15. The tubes 10 and 12 are coaxial and their common axis is vertical.

The tube 12 is surrounded by a resistance furnace 16 which here consists of three superposed stages 17, 18 and 19. Each stage comprises a heating resistance 20, 21 and 22, respectively generating temperatures of at least 1,500° C. Each stage has its own regulation means. The resistances are surrounded by respective refractory masses or rings 23, 24 and 25. The furnace 16 has a length equal to at least 10 times the diameter of tube 10.

The furnace is continued in its lower part by a cooling device 26, which comprises a body 27 with a flange 28, and surrounding that body a coil 29 in which circulates a cooling fluid.

The unit including the furnace 16 and the cooling device 26 is assembled in such a way that it can be moved, by means of a suitable drive mechanism (not shown), with respect to tubes 10 and 12 along a translation path parallel to the common axis of the tubes. The tube 10 is placed in a holder 30, cooled by circulating fluid as schematically represented by the two sections 31 and 32 on opposite sides of a partition element 33.

The operation is as follows:

The stages 17, 18, 19 of the furnace are adjusted in order to provide a temperature distribution along the axis of rod 11 as represented schematically by the diagram shown in FIG. 3.

On the left side of that FIGURE the rod 11 is represented in the same position as in FIG. 2. The arrow indicates the movement of rod 11 with respect to the heating stages 17, 18 and 19. On the right side of the diagram the curve D represents the temperature variation along the rod for a given position of the latter. In this diagram, the t axis is the temperature axis and the l axis represents the abscissae of the rod sections. Temperature t_f is the melting and solidification point of the material of the rod.

The temperature curve D can be divided into three sections:

- a section a having a steep slope, positive with respect to the l axis;
- a section b having a weak positive slope
- a section c having a very steep negative slope.

The intersection points of the curve D with the line passing through the point t_f and paralleling the abscissa determine on the rod the limits of the unmelted parts S_1 of the rod, of the liquid part L and of the resolidified part S_2 .

The particular shape, hereabove defined, of the temperature curve is obtained by giving to the melted zone L a large length (at least equal to the diameter of the rod) and operating the lower heating stage 17 at higher heating power than the other stages, taking into consideration the influence of the cooling devices.

A very steep temperature gradient is thus obtained across the solidification interface f , at the common boundary of the parts L and S of the rod. This gradient ranges from about 30° to 150° C per cm.

The apparatus hereinabove described also provides a perfect flat shape for said interface, so that the micro-

structure of the solidified part S_2 is accurately directed oriented parallel to the axis of the rod.

The unavoidable variations of the translation rate or of the heating power have no detrimental influence on the structure formed at the solidification interface, essentially because of the considerable mass of liquid matter placed above said interface. Thus, "band" formation which often occurs in directed single-crystal growth by moving a solidification interface is avoided.

Reference is now made to FIG. 4 showing another type of apparatus used in making metallic alloys according to the invention. Induction heating is used: the induction coil 40 surrounds an other tube 41 made of drawn quartz for example. Heating is achieved by means of a graphite tube 42, acting as a susceptor, which heats by radiation a refractory tube 43 in which the rod 11 to be treated is placed. The tube 43 is placed on a holder 44 which also acts as a cooler; its body is composed of a water-cooled solid-copper cylinder. Water is admitted through a central pipe 47 and then flows into an annular space 48 between pipe 47 and body 44.

The lower end of the outer tube 41 is cooled by water circulation in a channel 45.

An inert gas is admitted through an inlet 49 to the annular space 50, existing between the surrounding tube 41 and the graphite tube 42, and is exhausted through an upper outlet 51.

The unit including the furnace and the cooling device is vertically placed and enables movement of the rod with respect to the induction coil, by means of a suitable drive mechanism (not shown).

Good results have been obtained with a 250 mm long susceptor having a 16 to 18 mm diameter, surrounding a refractory tube of 8 to 12 mm diameter made of the alloy to be melted. The protective inert gas had a flow rate of 0.5 liter/minute. The constant translation rate of the beam supporting the assembly ranged from 1.18 to 30 cm/hour. The high-frequency generator had a frequency of 1 MHz. The induction coil had nine turns which were 1 cm apart. The regulation device enables a temperature control with a better than 1° C accuracy.

8. SPECIFIC EXAMPLES

The following are examples of alloys according to the invention.

EXAMPLE 1

The workpiece initially consists of a quaternary cast alloy whose composition (sgt percent) is as follows:

Co : 77 %
Ta : 12.2 %
CR : 10 %
C : 0.8 %

The workpiece is zoned by means of the apparatus shown in FIG. 4. The relative speed V of the rod is fixed at 1.2 cm/hour. The induction input is adjusted so that the length of the liquid zone is equal to or larger than five times the diameter of the rod, which is here 8 mm. For larger diameters, this ratio can be reduced to 1. Under these conditions, the thermal gradient normal to the solidification interface is about 150° C/cm.

Physico-chemical studies show that the final product is a matrix of cobalt-chromium solid solution, inside which are imbedded monocrystalline thread-like particles of tantalum carbide, TaC, perfectly lined up paral-

labeled to the rod axis. These particles are lamellae having a more or less regular polygonal shape.

The ratio of the lamellae to the cylinders depends on the operating conditions. In any event the smallest dimension of these particles ranges between 0.3 and 2 microns and their length is more than 3,000 times their smallest dimension.

The nature and the structure of the particles, on the one hand, and the composition of the solid-solution matrix, on the other hand, give the material an excellent tensile strength at high temperatures (about 40 hbars at 1,000° C).

The breaking time, under flow, at 1,000° C and under a stress of 10.5 hbar is 700 hours in air. At 1,050° C under 11 hbar, the breaking time under vacuum is 2,500 hours.

According to the properties intended for the material, the chromium concentration of the solution and also, to a certain extent, the carbide concentration of the rod can be varied to a large extent.

Very good results are obtained because of the "plateau" shape of the Co-Cr phase diagram for high chromium concentration as will be seen in the following examples.

EXAMPLE 2

The workpiece has the following starting composition (wtg percent):

Co : 72 %
Cr : 15 %
Ta : 12.2 %
C : 0.8 %

The operation is carried out as indicated in Example 1 hereinabove, but with a movement rate *V* of 2.5 cm/h. The final material has excellent mechanical properties at high temperatures as well as at room temperature. On tensile tests, at room temperature, the yield point is 100 hbar, the ultimate tensile strength *R* is 115 hbar and the elongation at rupture is 20 percent (FIG. 8). The fatigue strength at 10^7 cycles in rotative bending is ± 63 hbar.

At high temperatures, such a material exhibits a good mechanical strength and corrosion resistance.

On flow tests in air, the breaking time at 1,000° C under 10.5 hbar is 1,850 hours.

At 800° C : *R* = 70 hbar
and at 1000° C : *R* = 40 hbar.

Such a material has also at room temperature, besides a high mechanical strength, a very good ductility.

This latter property is probably due to the fact that the structure of the reinforcement phase lets it play entirely its part, said phase occupying a rather small volume of the matrix which consequently imparts to a piece made of such an alloy a substantial deformation capacity before breaking.

The operating conditions of the furnace can be modified to quite a large extent. Thus the movement rate of the solidification interface can be adjusted to a value ranging from 1 to 15.5 cm/hour.

As for the thermal gradient, normal to the solidification interface, its value can be lowered to 30° C/cm in certain cases, with, still interesting results.

The chromium concentration of the matrix, the movement rate of the solidification interface and the thermal gradient at the interface can be adjusted in order to have the reinforcement phase consist almost exclusively of cylinders, or two-dimensional lamellae, or triple-branched lamellae, as shown on photomicrographs of FIGS. 9a and 9b (X 2900) which show the influence of an addition of a 15 percent amount of chromium upon the carbide whiskers. FIG. 9a is a scanning electron photomicrograph taken after electrolytic selective etching of the matrix revealing the whiskers, taken at an angle, for an alloy whose composition is:

Cobalt : 87 % by weight
Tantalum: 12.2 % by weight
Carbon : 0.8 % by weight

(The latter alloy, for comparison, was unidirectionally solidified by zoning in the apparatus of FIG. 1 at a movement rate *V* of the solidification interface of 5.25 cm/hour and a thermal gradient *G* at the interface of about 500° C/cm, the length of the liquid zone being approximately equal to the bar diameter. A photomicrograph of the cross-section is shown in FIG. 5 (X 780); when the rate was increased to *V* = 15.75 cm/hour the cross-section after electrolytic etching had the photomicrograph (X 4,000 with scanning electron microscope) of FIGS. 6).

FIG. 9b is a similar photomicrograph for an alloy whose composition corresponds to that of Example 2 with a rate *V* adjusted to 1.2 cm/hour.

EXAMPLE 3

The operation is carried out as in the preceding Example, the composition being as follows (weight percent):

Co : 72 %
Cr : 15 %
Nb : 11.5 %
C : 1.5 %

By unidirectional solidification at a rate *V* adjusted to 1.15 cm/hour, a final product is prepared which is made of a chromium-cobalt matrix in which irregular whiskers and lamellae of a niobium carbide reinforcement phase are imbedded, as shown in FIG. 10 which is an optical photomicrograph of a normal cross-section (X 780).

In accordance with our invention, also, the metal or metals forming the carbide or carbides of the reinforcement phase are incorporated in excess in the composition of the starting alloy, to form one or several addition elements in the matrix, as shown in the three following examples:

EXAMPLE 4

The workpiece consists originally of a quaternary alloy having the following composition (weight percent):

Ni : 74 %
Ta : 15.2 %
Cr : 10 %
C : 0.8 %

This workpiece is zoned by the unidirectional-solidification method, the interface moving at the rate of 1.2 cm/hour.

An alloy is obtained whose structure is shown on the photomicrograph of FIG. 11 (X 3,000), taken at an angle after selective electrolytical etching, and whose reinforcement phase whiskers have approximately square sections. The alloy is a nickel-chromium-tantalum solid-solution matrix in which are imbedded long-sized monocrystalline particles of tantalum carbide. The matrix, which includes the excess of tantalum not combined with carbon into tantalum carbide, has a higher hardness than a nickel-chromium solid solution having proportions of nickel and chromium similar to those of matrix consisting of only these two components.

In the following Example the nickel-solid-solution-based matrix is reinforced by niobium carbide:

EXAMPLE 5

The workpiece has the following starting composition (weight percent):

Ni : 72 %
Cr : 10 %
Nb : 16.85 %
C : 1.15 %

After zoning as described in the foregoing Example, a compound is obtained whose long-sized carbide whiskers also have a cylindrical shape, as shown in FIG. 12 (X 5,500) which is an electron photomicrograph taken at an angle of 40° with respect to the axis of the rod and with a scanning microscope after partial extrication of the whiskers by electrolytic selective etching of the matrix.

The thus-prepared alloy is a matrix whose hardness is higher than that of a nickel-chromium solid solution having proportions of nickel and chromium similar to those of a solid solution consisting of only these two components.

EXAMPLE 6

The workpiece has the following starting composition (weight percent):

Ni : 76.5 %
Cr : 10 %
Ti : 12.2 %
C : 1.3 %

By the unidirectional-solidification method described above, an alloy is prepared in the form of a nickel-chromium matrix in which long-sized monocrystalline particles of titanium carbide are imbedded.

The properties of this alloy are particularly remarkable because on the one hand the titanium carbide, whose expansion coefficient is close to that of the matrix, forms a reinforcement phase which prevents stress formation at the matrix reinforcement-phase interfaces, and, on the other hand the excess titanium forms a dispersed compound Ni_3Ti which increases the matrix hardness and whose dispersion can be improved by a structural precipitation treatment.

Although the introduction in excess of carbide-forming metals in Examples 4, 5 and 6 above leads to overall compositions which slightly deviate from eutec-

tic compositions, the structures obtained remain of the eutectic type.

Because of the closely similar cobalt, nickel and iron properties, it is also possible to prepare alloys wherein a transition-metal carbide forms a reinforcement phase imbedded in a solid-solution matrix, for instance a Ni—Co—Cr or Ni—Fe—Cr matrix.

The composition is advantageously so chosen, for such alloys, as to yield a matrix constituted by an austenitic solid solution.

Note that "austenitic solid solution" taken in its most general sense, means a solid solution based on iron and/or nickel and/or cobalt which crystallizes in the face-centered-cubic lattice.

EXAMPLE 7

The workpiece has the following starting composition (weight percent):

Co : 57 %
Cr : 20 %
Ni : 10 %
Ta : 12.2 %
C : 0.8 %

The workpiece is unidirectionally solidified by means of the apparatus described with reference to FIG. 4, at a solidification rate of 1.2 cm/hour.

The final product is a Co—Ni—Cr solid-solution matrix, having a face-centered cubic structure, in which long-sized monocrystalline rod-like and/or platelet-like lamellae of tantalum carbide are imbedded. The matrix keeps its austenitic structure for temperature values ranging from room temperature to its melting point. The structure of the alloy is shown in FIG. 13 which is a scanning electron photomicrograph (X 1,900) taken at an angle of 40°.

The mechanical characteristics of such an alloy are the following:

— at room temperature:
Ultimate tensile strength R = 107 hbar
Elastic limit E = 96 hbar
Total elongation A% = 30 %
— at 1000°C:
R = 40 hbar.

Besides, this alloy has a very good resistance to dry corrosion, as shown by thermogravimetry, indicating a weight increase of 1 mg/cm² after 17 hours heating at 1,000° C in air.

The weight increase follows a law as shown by the graph of FIG. 14 in which the ordinates indicate the weight increase in mg/cm², time being plotted on the abscissae.

Comparative tests have been conducted with the alloy of the invention and other refractory known alloys such as those known as IN 100 (cast) and UDI-MET 700 (forged).

i. Shock bending

The tests have been conducted at 20° C, 700° C, and 1,000° C on cylindrical test pieces with a Wolpert Feston PW5 hammer-machine.

The results of the tests are summarized in the following table A which shows the advantages of the alloy according to the invention.

TABLE D

Test temperature		Stress (hbar)	Time in hours (t)		K=T(20+log t) 10 ⁻³	
°C	°K (T)		for elongation		at	for
			%		rupture	A% = 0.5
				0.2	0.5	
800	1073	30			>4000	>25.4
800	1073	35			225	24
950	1223	20			1363	28.3
1000	1273	15	1500	1850	2000	29.6
1000	1273	18	90	350	>350	28.7
1000	1273	20			133	28.2
1030	1303	14	410	1150	1200	30.1
1070	1343	12	31	145	170	29.9
1100	1373	10	1100	1200	1200	31.7
1150	1423	10	30	70	>100	31.1

TABLE A

Alloy	Temperature °C	Resilience da J/cm2
Alloy of the invention	20	>21
UDIMET 700	20	11
IN 100	20	6
Alloy of the invention	700	>21
UDIMET 700	700	10
IN 100	700	4.5
Alloy of the invention	1000	>21
UDIMET 700	1000	20
IN 100	1000	2.5

ii. Thermal fatigue

Wedge shaped test pieces are placed in the flame of an air-propane burner in order that the edge of the test piece be brought to 1,100° C and stays at this temperature during 60 seconds. The test piece is then withdrawn from the flame and cooled in 20 seconds to 300° C by a cold air stream.

A test piece made of the alloy according to the invention was subjected to a 300 cycles test. The first fatigue crack appears after 100 cycles and its propagation is relatively slow. The same test carried on good refractory nickel base alloys such as IN 100 or PD 16 results in the first fatigue crack appearing after 10 to 20 cycles and the propagation is much quicker than with the alloy according to the invention.

Further tests have also been carried out namely fatigue test and flow stress test.

The results of these tests are summarized in the following tables:

iii. fatigue test

— at room temperature the fatigue strength in rotative bending (49 Hz) is:

TABLE B

Alternate stress (hbar)	Number of cycles
± 60	>10 ⁷
± 65	>10 ⁷
± 70	rupture

— at 800° C the fatigue strength under ondulated traction (87 Hz) is as below:

TABLE C

Stress mini	maxi	Number of cycles
2	40	>10 ⁷
2	45	rupture

iii. flow stress test

The results are summarized in Table D

15 The two last columns refer to the values of the Larson-Miller index "K" defined by $K = T(20 + \log t)10^{-3}$ wherein T is the temperature in °K and t the duration of the test measured in hours. The indicated values of this index emphasise the good characteristics of the alloy according to the invention.

EXAMPLE 8

The workpiece has the following starting composition (weight percent):

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Co : 62%
Cr : 20%
Ni : 10%
Nb : 7.1%
C : 0.9%

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With the same directional-solidification method as described in the foregoing Example, an alloy is prepared whose structure, as shown in FIG. 15 which is an optical microphotograph of a cross-section of the sample (X 780), is a matrix consisting of a face-centered-cubic Co—Ni—Cr solid solution in which long-sized monocrySTALLINE niobium carbide particles are imbedded.

40 At 1,000° C, the U.T.S. of such an alloy is 44.5 hbar.

The cobalt of the solid solution can also be replaced by iron, a metal belonging like the former to group VIII of the fourth period of the Mendeleiev Chart. A material displaying very interesting characteristics as regards dry corrosion can be prepared as follows:

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EXAMPLE 9

The workpiece has the following starting composition (weight percent):

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Fe : 48.5%
Cr : 22 %
Ni : 17.5%
Ta : 11.25%
C : 0.75%

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The alloy which is thus prepared, whose structure is shown in FIG. 16 which is an electron photomicrograph (X 5,800), consists of tantalum carbide whiskers imbedded in an austenitic Fe—Cr—Ni matrix particularly corrosion-resistant at high temperatures, as determined by thermogravimetric tests showing a weight increase of 0.8 mg/cm2 after 17 hours heating at 1,000° C in air. The weight increase follows the law shown by the diagram of FIG. 17.

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EXAMPLE 10

Operating as in the previous Examples, but replacing tantalum by hafnium (either totally or partially) inas-

much as the carbides of these two metals are miscible in any proportions, yields a reinforcement phase of monocrystalline particles of mixed single-phase carbides, TaC—HfC.

The workpiece has the following starting composition (weight percent):

Co : 57%
Cr : 20%
Ni : 10%
Ta : 9.7%
Hf : 2.5%
C : 0.8%

The structure of the material prepared by the method just described, at a rate *V* of 1.2 cm/hour, is shown in the electron photomicrograph represented in FIG. 18 (X 5,800).

It is to be noted that the crystalline-phased solid solution corresponding to 80 percent of TaC and 20 percent of HfC is at the present time the most refractory mixed crystal known (melting point of about 3,940°C).

According to our invention, also, an additional element is introduced into the alloys prepared as hereabove described, this element improving the mechanical properties of the matrix by a subsequent thermal treatment or by precipitation on solidification. Thus in the nickel-based alloys aluminum is added in a proportion ranging from 2 to 6 percent.

Examples of such alloys are as follows:

EXAMPLE 11

The workpiece has the following starting composition (weight percent):

Ni : 70 %
Ta : 16.3 %
Cr : 10 %
C : 0.7 %
Al : 3 %

By unidirectional solidification, an alloy is prepared in which the excess tantalum is dissolved in the matrix inside which the tantalum carbide reinforcement phase is imbedded, and which comprises an intermetallic complex compound of the γ' type, appearing on cooling after solidification; its dispersion can be improved by a structural precipitation treatment.

The structure of such a material is shown in FIG. 5 which is an electron microphotograph taken at an angle of 24° (x 5,200). It can be seen that the carbide whiskers having a square section are imbedded in the complex matrix containing the hardening precipitate γ' . The photomicrograph shows the structure after rough-solidification, but the latter can be refined by thermal treatments.

Direct observation by transmission electron microscopy shows, as evidenced in FIG. 6 (X 27,000), the particular shape of the γ' -type precipitate and the dislocations existing in the matrix.

Before any treatment, this material as a U.T.S., at room temperature of 125 hba (178 × 10³ psi) with 10 percent elongation.

EXAMPLE 11a

The workpiece has the following starting composition (weight percent):

Ni : 53.6 %
Co : 20 %
Ta : 131 %
Cr : 10 %
C : 0.4 %
Al : 3 %

The alloy obtained in this example has a structure similar to that of Example 11 but differs therefrom by the replacement of part of the nickel by cobalt. Immediately beneath the solidus this alloy is constituted by an austenitic matrix of Ni, Co, Cr, Al, into which are imbedded reinforcement fibers of tantalum carbide.

During the cooling a γ' phase of Ni—Al compound precipitates in the dispersed state. Dispersion can be improved by an homogenization thermal treatment of 1 hour at 1,150°C followed by a structural precipitation treatment of 24 hours at 760°C.

The tests carried out on this alloy are summarized in the following tables:

TABLE E

Solidification rate (cm/hour)	(at room temperature) Thermal treatment	UTS (hbar)	Elongation at rupture (%)
2.36		144	9.5
3.50		149.5	7
2.36	(1)	146	12.8
3.50	(2)	146.5	9.2
2.36	(2)	161	11.2
3.50	(2)	166	4.1

Thermal treatment: (1): homogenization: 1 hour at 1150°C
(2): (1) + structural precipitation treatment 24 hours at 760°C

TABLE F

Solidification rate (cm/hour)	(at different temperatures) Thermal Treatment	Test temperature (°C)	UTS (hbar)	Elongation at rupture (%)
2.36	without	760	85	9
2.36	(2)	760	98.5	10.8
2.36	without	1000	35.2	
2.36	without	1000	33.2	8.3
2.36	(2)	1000	41.3	4.45

Thermal treatment: (1): homogenization: 1 hour at 1150°C
(2): (1) + structural precipitation treatment 24 hours at 760°C.

TABLE G

Thermal Treatment	Test	Test Temperature	Stress (hbar)	Number of cycles
without	Rotative binding (49 Hz)	20°C	± 45	> 10 ⁷
do.	do.	do.	± 50	rupture
(2)	do.	do.	± 45	> 10 ⁷
(2)	do.	do.	± 50	rupture
without	Ondulated traction (87 Hz)	800°C mini 2, maxi 60		> 10 ⁷
do.	do.	800°C mini 2, maxi 65		rupture

Thermal treatment: (1): homogenization: 1 hour at 1150°C.
(2): (1) + structural precipitation treatment 24 hours at 760°C.

TABLE II

Thermal Treatment	Test Temperature		Stress (hbar)	(Flow stress tests) Time in hours (t)		$K=T(20+\log t) 10^{-3}$	
	(°C)	(°K) T		for elongation A : 0.5	to rupture	for A = 0.5%	to rupture
without	760	1033	60	2	40	21	22.3
(2)	760	1033	60	96	760	22.6	23.6
without	850	1123	40	6	8	23.4	23.5
(2)	850	1123	40	35	142	24.2	24.8
without	1000	1273	15	351	483	28.7	28.8
(2)	1000	1273	15	43	1020	27.5	29.3
without	1030	1303	12	69	70	28.5	28.5
(2)	1030	1303	12	69	316	28.5	29.4
without	1070	1343	12	14	15	28.5	28.4
(2)	1070	1343	12	34	34	29	29

Thermal treatment: (1): homogenization: 1 hour at 1150°C
 (2): (1) + structural precipitation treatment 24 hours at 760°C.

*As defined in table D.

EXAMPLE 12

The workpiece has the following starting composition (weight percent):

Ni : 72 %
 Cr : 10 %
 Nb : 14.3 %
 Al : 3 %
 C : 0.7 %

After zoning, an alloy is obtained whose structure is similar to that of the foregoing example, but in which tantalum is replaced by niobium.

EXAMPLE 13

The workpiece has the following starting composition (weight percent) :

Ni : 76.5 %
 Ti : 8.2 %
 Cr : 10 %
 C : 1.3 %
 Al : 4 %

After treatment by the described method, at a relative speed of 2.5 cm/hour, an alloy is obtained which contains a titanium carbide reinforcement phase, imbedded in a nickel-chromium matrix comprising an inter-metallic compound $Ni_3(Ti,Al)$, which has a face-centered-cubic structure, and whose dispersion can be improved by a structural precipitation treatment. FIG. 7, which is a scanning electron photomicrograph (X 2,300) taken at an angle of 40°, shows the structure of the reinforcement phase containing finely dispersed point-like carbide particles, and also the γ' -type precipitate as it appears on rough solidification.

While a critical characteristic of the alloys of the present invention is the exclusion of chromium in the reinforcement phase, it should be observed that up to 25 percent by weight of chromium may be present in solid solution in the matrix phase where the latter is primarily a cobalt-based system and up to 45 percent by weight in solid solution in the matrix phase where the latter is primarily a nickel-based system. Where mixtures of cobalt and nickel constitute the matrix phase, the chromium may be present in an amount of 25 percent by weight of the cobalt + 45 percent by weight of the nickel, as a maximum. In the foregoing Examples

(4, 5, 6, 11, 12 and 13), dealing with a nickel-chromium matrix, the alloys contain about 85% by weight of the matrix-forming elements and about 15 percent by weight of carbide-forming elements so that a maximum of 45 percent by weight of chromium in the matrix phase corresponds to alloys containing up to 37 percent by weight chromium.

We have used herein the terms "rod-like" and "platelet-like lamellae" to describe the elongated monocrystalline particles constituting the reinforcement phase and we intend the term "monocrystalline," therefore, to comprehend both fibrous and flattened reinforcement particles.

The alloys of the present invention have proven to be especially effective for use in high-temperature gas turbines for aeronautical applications, in terms of mechanical resistance to high temperatures, resistance to material fatigue, high corrosion resistance and exceptional mechanical strength on a long-term basis.

We claim:

1. A refractory directionally solidified polyvariant fiber-reinforced composite having eutectic-type structure consisting essentially of two distinct independent phases constituted by:

a. a complex multicomponent matrix phase consisting essentially of:

- at least one metal selected from the group consisting of Fe, Ni and Co, and
- chromium in an amount between 10 and 25 percent by weight of the composite;

and in said matrix:

b. an in situ grown reinforcing phase free from chromium and consisting essentially of whisker-like elongated monocrystalline fibers of at least one metal monocarbide, the metal of which is selected from the group constituted by Ta, Nb, Hf and Ti.

2. A refractory directionally solidified composite as defined in claim 1 wherein said metal of the monocarbide includes tantalum in an amount of 10 to 18 percent by weight of the composite.

3. A refractory directionally solidified composite as defined in claim 1 wherein said metal of the monocarbide includes titanium in an amount of 8 to 12 percent by weight of the composite.

4. A refractory directionally solidified composite as defined in claim 1 wherein said metal of the monocarbide includes niobium in an amount of 7 to 17 percent by weight of the composite.

5. A refractory directionally solidified composite as defined in claim 1 wherein said matrix phase is an austenitic solid solution.

6. A refractory directionally solidified composite as defined in claim 5 wherein said matrix phase is made of cobalt, chromium and up to 10 percent by weight of the composite of nickel or iron, whereby any detrimental allotropic transformation of the Co base matrix is avoided.

7. A refractory directionally solidified composite as defined in claim 5 wherein said matrix phase is made of iron, chromium and up to about 20 percent by weight of the composite of nickel.

8. A refractory directionally solidified composite as defined in claim 5 wherein said matrix phase is made of nickel, chromium and up to 20 percent by weight of the composite of cobalt, whereby a greater volume fraction of fibers is allowed.

9. A refractory directionally solidified composite as defined in claim 1 wherein said matrix phase includes at least one metallic addition element other than Fe, Ni, Co and those forming said monocarbide, said addition element forming a second reinforcing phase consisting of an intermetallic compound with a metal of the matrix phase by solid state thermal treatment.

10. A refractory directionally solidified composite as defined in claim 9 wherein said addition element is alu-

minum in an amount of substantially 2 to 6 percent by weight of the composite.

11. A refractory directionally solidified composite as defined in claim 9, wherein said second reinforcing phase is in the form of substantially point-like particles dispersed in said matrix.

12. A refractory directionally solidified composite as defined in claim 8 wherein said matrix phase further comprises a γ' type precipitate of nickel and aluminum.

13. A refractory directionally solidified composite as defined in claim 6 wherein said matrix phase contains also at least one of the monocarbide forming metals.

14. A refractory directionally solidified composite as defined in claim 8 wherein said matrix phase contains also at least one of the monocarbide forming metals.

15. A refractory directionally solidified composite as defined in claim 1 wherein said reinforcing phase is a single-phased solid solution consisting of 80 percent by weight tantalum carbide and 20 percent by weight hafnium carbide.

16. A refractory directionally solidified composite as defined in claim 1 wherein said fibers have a smallest transverse dimension of substantially 0.3 to 2 microns and a length at least equal to 3,000 times their smallest transverse dimension.

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