Sept. 15, 1970 F. D. LEMKEY ET AL 3,528,808

MONOCARBIDE REINFORCED EUTECTIC ALLOYS AND ARTICLES

Filed Oct. 11, 1967 6 Sheets-Sheet 1

FIG. 1

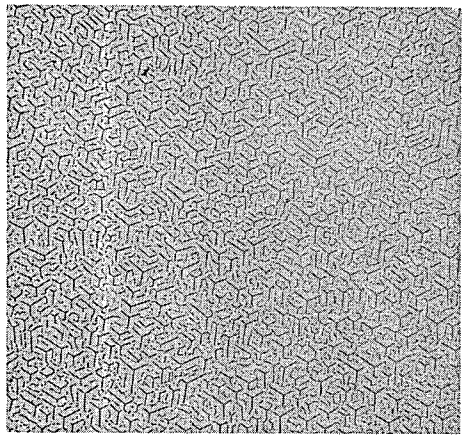
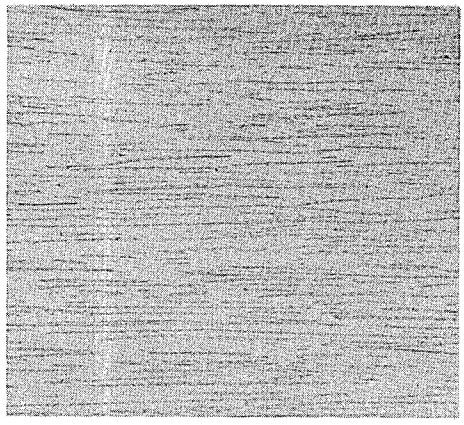


FIG. 2

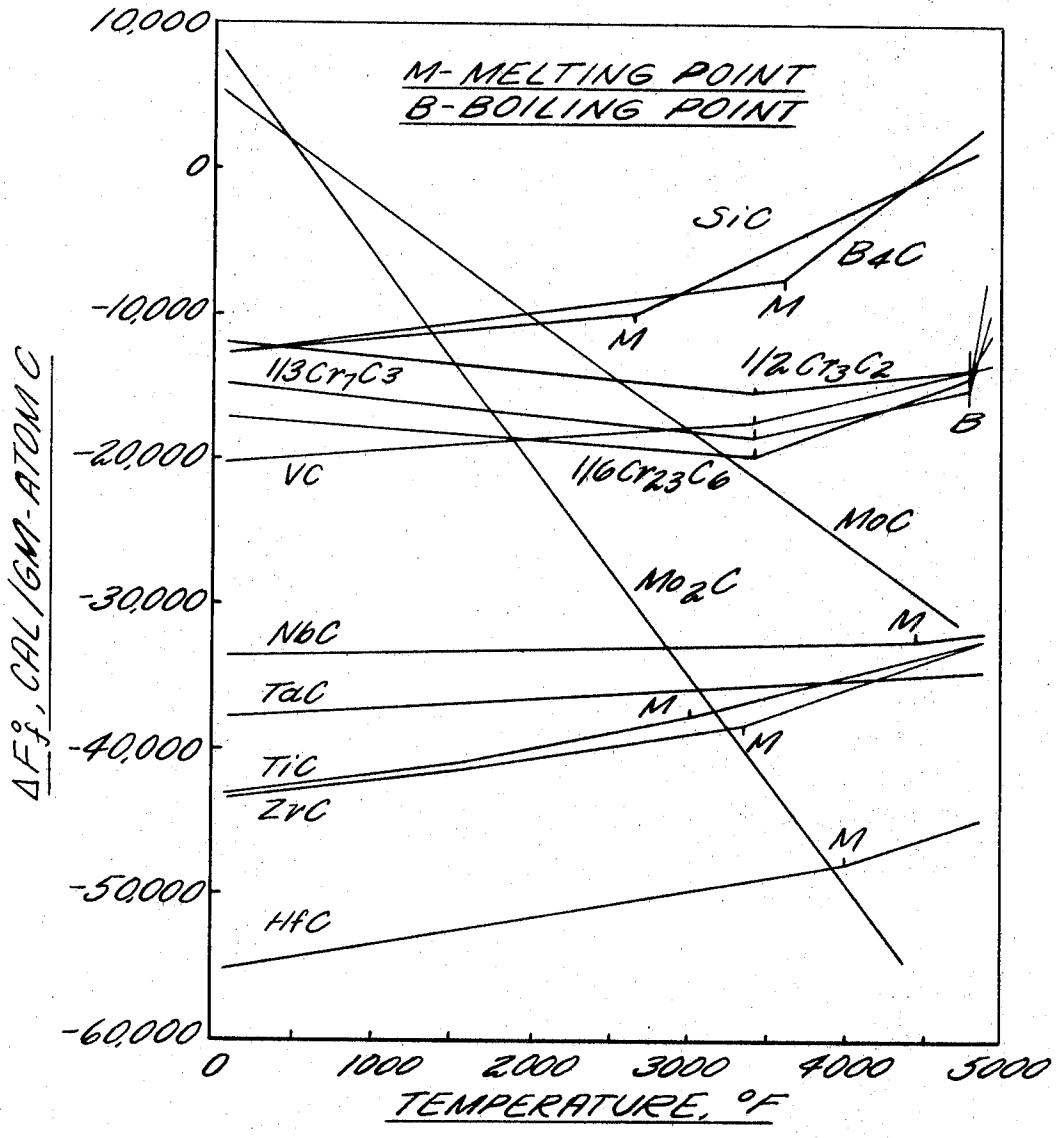


INVENTORS
FRANKLIN D. LEMKEY
EARL R. THOMPSON
BY Richard N. James.
ATTORNEY

MONOCARBIDE REINFORCED EUTECTIC ALLOYS AND ARTICLES

Filed Oct. 11, 1967 6 Sheets-Sheet 3

FIG. 3

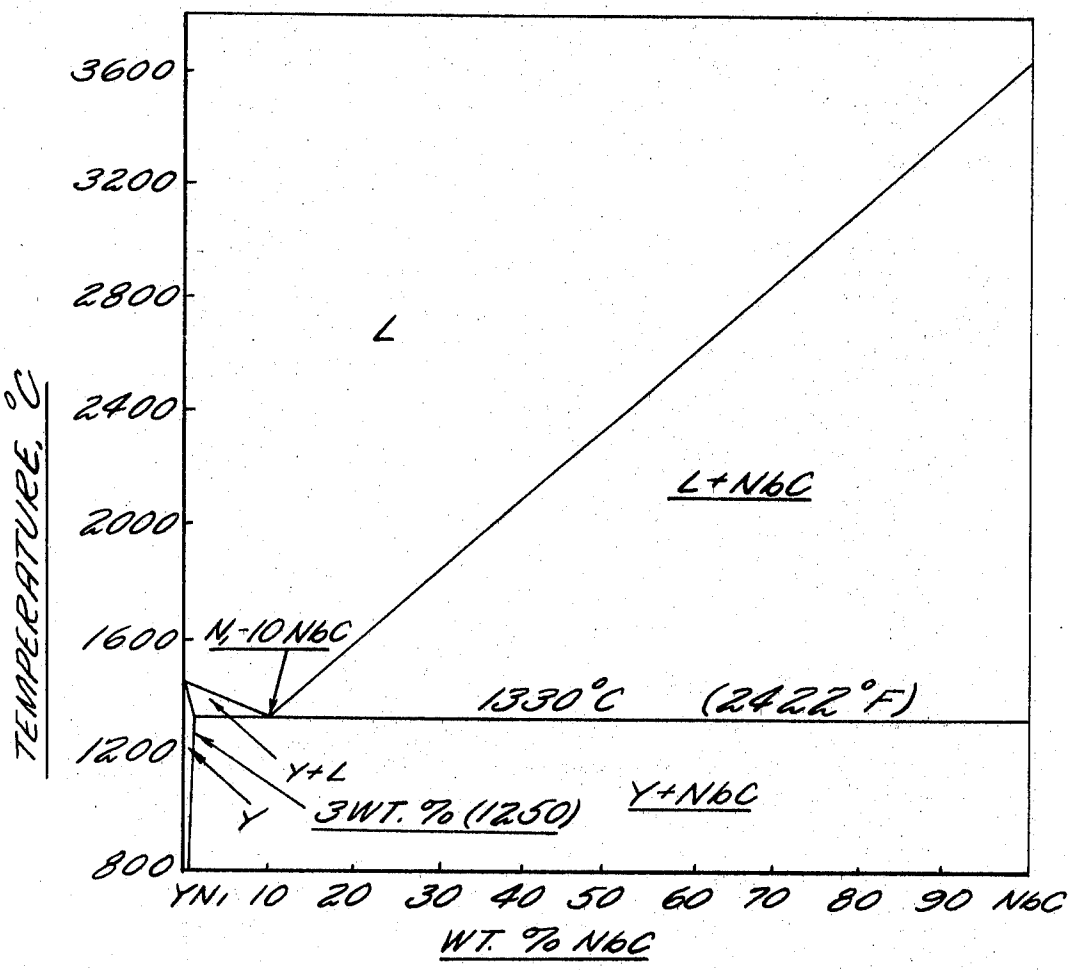


STANDARD FREE ENERGIES OF FORMATION OF THE CARBIDES PER GRAM-ATOM OF GRAPHITE

MONOCARBIDE REINFORCED EUTECTIC ALLOYS AND ARTICLES

Filed Oct. 11, 1967 6 Sheets-Sheet 3

FIG. 4



CONSTITUTIONAL DIAGRAM OF Ni-N6C

MONOCARBIDE REINFORCED EUTECTIC ALLOYS AND ARTICLES

Filed Oct. 11, 1967 6 Sheets-Sheet 4

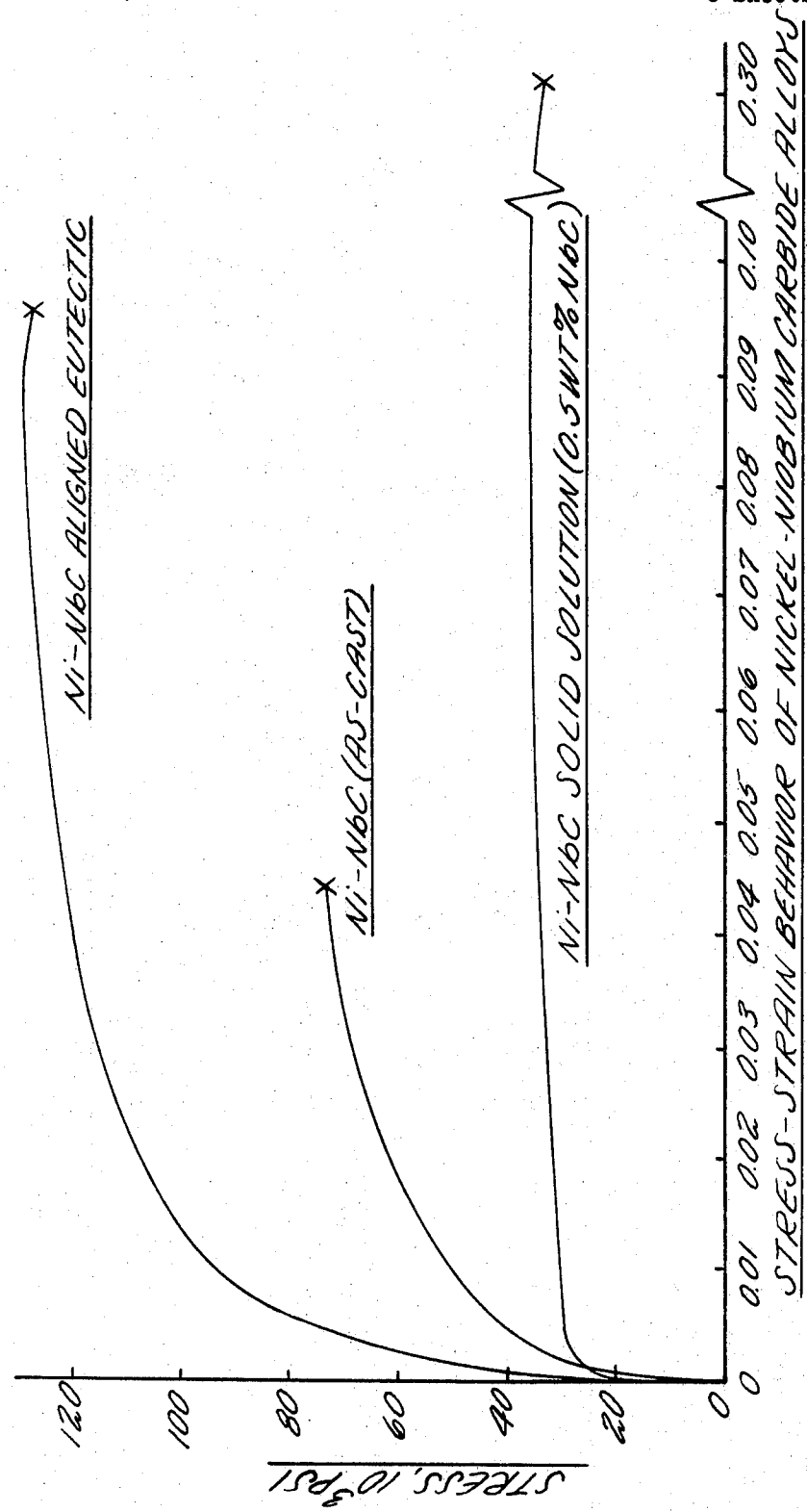
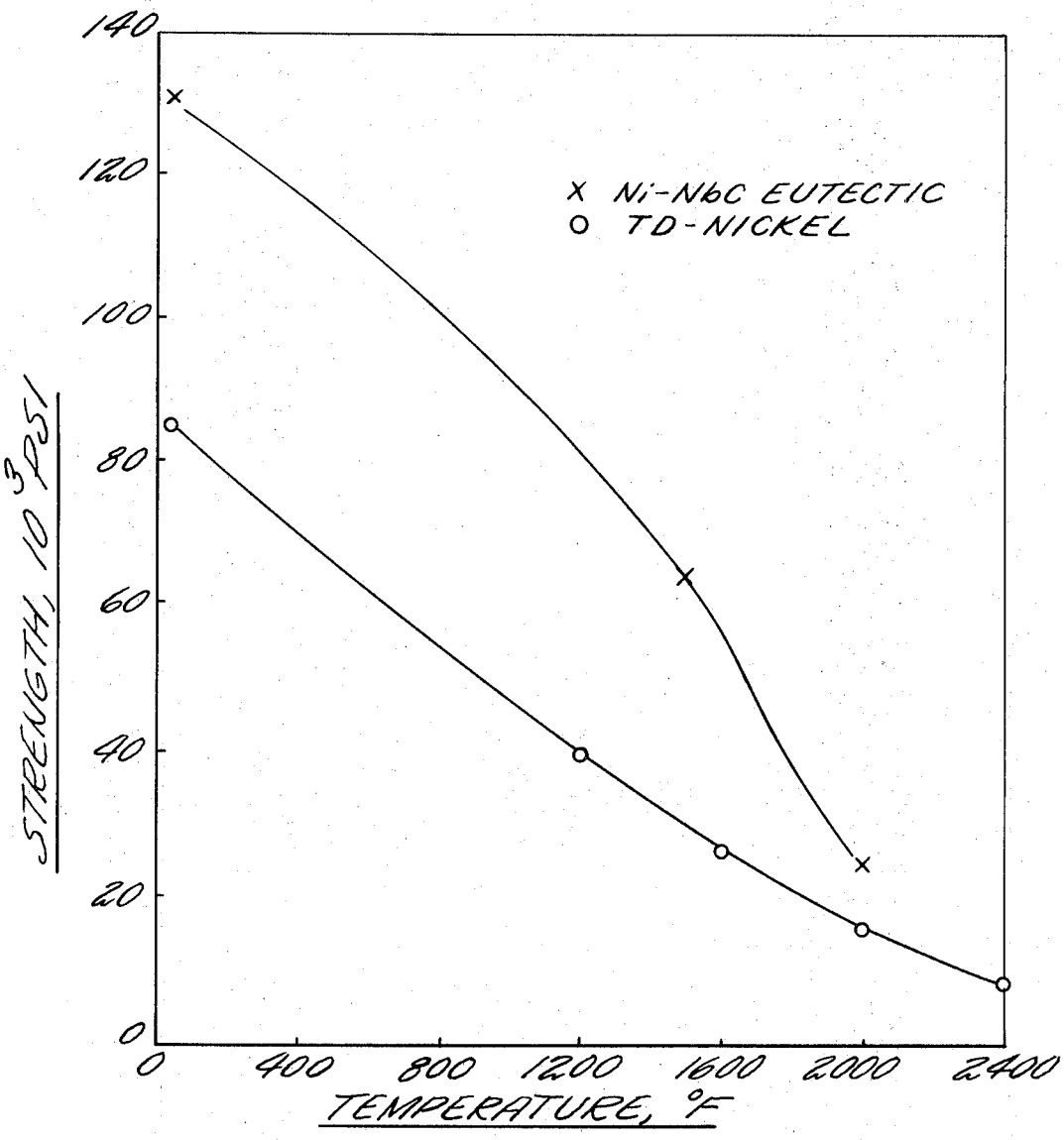


FIG. 5

FIG. 6



TENSILE STRENGTHS AS FUNCTION OF TEMPERATURE

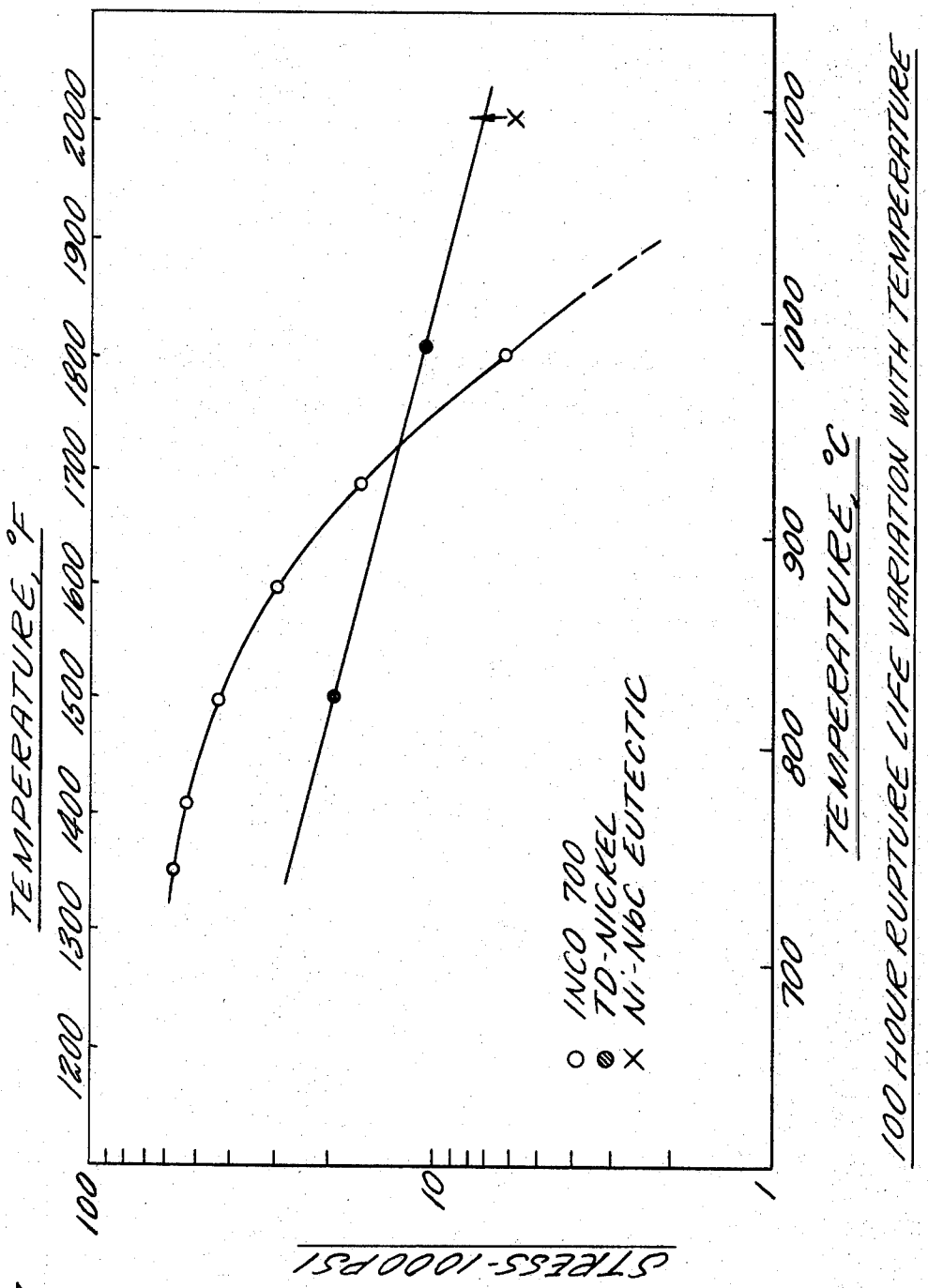

TEMPERATURE, °F
1200
1300
1400
1500
1600
1700
1800
1900
2000
TEMPERATURE, °C
700
800
900
1000
1100
STRESS-1000 PSI
100
10
1
INCO 700
TD-NICKEL
Ni-NbC EUTECTIC
100 HOUR RUPTURE LIFE VARIATION WITH TEMPERATURE

FIG. 7

United States Patent Office 3,528,808 Patented Sept. 15, 1970

3,528,808

MONOCARBIDE REINFORCED EUTECTIC ALLOYS AND ARTICLES

Franklin D. Lemkey and Earl R. Thompson, Glastonbury, Conn., assignors to United Aircraft Corporation, East Hartford, Conn., a corporation of Delaware

Filed Oct. 11, 1967, Ser. No. 674,607
Int. Cl. C22c 19/00
U.S. Cl. 75—170 8 Claims

ABSTRACT OF THE DISCLOSURE

Alloys of cobalt, nickel or chromium with a monocarbide from the group of monocarbides of titanium, zirconium, hafnium, vanadium, niobium, and tantalum in the form of a pseudo-binary eutectic are described, particularly as unidirectionally solidified.

BACKGROUND OF THE INVENTION

The present invention relates in general to the nickel, cobalt and chromium base alloys, particularly those alloys having utility in gas turbine engine applications.

To increase the thrust and performance characteristics of the advanced gas turbine engines, the scheduled turbine inlet temperatures thereof have been revised upwardly to and even beyond the temperature capabilities of the conventional nickel and cobalt base superalloys. Engine components fabricated from these conventional alloys continue to find utility in engine use because there are no satisfactory alternatives currently available and only, in more severe environments, because of the incorporation of schemes like internal component cooling to hold the alloys within acceptable temperature limits notwithstanding the temperature of their environment. Although significant advances in uncooled engine parts may eventually evolve from the use of the refractory metal alloys, these alloys in general are inherently susceptible to a rapid and destructive oxidation-erosion, and coatings for these alloys which will provide adequate resistance to gas-metal attack in a jet engine system for the necessary thousands of hours are not currently available.

In an attempt to provide an interim solution to the materials problem in the time interval between the phase-out of the conventional nickel and cobalt base alloys and the introduction of a satisfactory refractory metal system, present attention is concentrated in the dispersion-strengthened nickel and cobalt base alloys, such as TD nickel (98% nickel, 2% thoria). However, while the superiority of the TD nickel to the conventional superalloys is clear at 2000° F. and above, this superiority is achieved only at the sacrifice of strength at 1800° F. and below, low ductility at elevated temperatures, and reduced fabricability and corrosion resistance.

SUMMARY OF THE INVENTION

The invention described herein relates to alloys of nickel, cobalt and chromium together with a monocarbide whose metal element is selected from the Periodic Table Group IV*a* or V*a*, and articles produced therefrom. More particularly, there is described herein a class of alloys distinguishable as eutectic compositions between nickel, cobalt and chromium and a monocarbide of titanium, zirconium, hafnium, vanadium, niobium or tantalum, each

of which solidifies as a face-centered cubic crystal, each of the pseudo-binary eutectics responding to unidirectional solidification (as taught by Kraft 3,124,452, for example) so as to form an ordered microstructure comprising generally parallel rods or lamellae of the predominantly carbide phase embedded within a metal solid solution matrix. An ordered microstructure of this nature is hereinafter referred to as fibrillar, and the reinforcing phase as fibrous.

The described alloys and the articles formed therefrom not only exhibit strengths comparable to TD nickel at 2000° F., but they also display a marked superiority thereto in the temperature regimes below 1800° F.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a photograph of the microstructure of a Ni-NbC eutectic specimen which is unidirectionally solidified at a rate of 2.8 cm./hr. The photograph is taken transverse to this axis of solidification.

FIG. 2 is a photograph of the microstructure of a Ni-NbC specimen, unidirectionally solidified at a rate of 2.5 cm./hr., the photograph showing a longitudinal section. The fibrous phase is predominantly carbide.

FIG. 3 is a graph on which the standard free energies of formation of a number of carbides are plotted as a function of temperature.

FIG. 4 is a postulated constitutional diagram for the Ni-NbC system.

FIG. 5 is a graph illustrating the stress-strain behavior of the Ni-NbC alloys.

FIG. 6 is a plot of rupture life variation with temperature for the Ni-NbC aligned eutectic as compared to other competitive materials. The Ni-NbC specimen did not fail in 258 hours.

FIG. 7 is a comparison of tensile strength as a function of temperature of TD nickel and the Ni-NbC aligned eutectic.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Based on mechanical demands alone, the failure of the current nickel and cobalt base alloys to satisfy the criteria imposed by the operating conditions of the projected advanced gas turbine engines is understandable, since service temperatures of 200° F. or less below their incipient melting points are anticipated, and the alloy microstructures are often adversely affected at such temperatures. The effectiveness of particle strengthening and solid solution strengthening is also substantially reduced because thermal activation brings about an increase in the ease of dislocation movement past pinning or retarding barriers, thereby resulting in an undesirable plastic deformation.

A promising group of materials for structural applications at elevated temperatures are the fiber strengthened metal-matrix composites. The mechanical properties of these materials are such that their strength is largely dependent upon the volume fraction and the properties of the unidirectionally-aligned fibrous reinforcement, with the continuous metallic matrix serving as the load transfer medium and contributing toughness to the composite. Significant high-temperature strengths are attained if the reinforcing phase is strong and the microstructure of the composite is stable at elevated temperatures.

The incorporation of a high modulus reinforcement in a lower modulus metal matrix also results in a material that is less susceptible to fatigue failure, since

fatigue is a strain controlled process. This has been observed, for example, in the boron-filament-reinforced aluminum composite system.

In the usual process for forming the fiber reinforced composites, the reinforcing medium is normally provided in filamentary form and the matrix material is cast or pressed around the filamentary reinforcement. The glass filament-resin matrix art reveals numerous methods by which the composites may be formed.

It is now known that particular material systems, including certain of the eutectics, may be unidirectionally solidified to form ordered microstructures wherein a phase solidifies from the melt in the form of parallel rods embedded in a matrix phase. If the fibrous phase of the controlled eutectic thus solidified is selected to provide the desired high strength, high modulus reinforcement in the lower modulus matrix, the resulting structures would have immediate utility. It is known that the above-mentioned controlled eutectics have preferred crystallographic interfaces of presumed low energy and hence stable microstructures. Accordingly, exposure of these microstructures to high temperatures for long periods of times does not result in significant coarsening. Furthermore, since all the phases are in equilibrium, the eutectic composites do not suffer from chemical incompatibility, such as that present in composites fabricated by some of the other methods, which can lead to a serious degradation of the mechanical properties of the structure.

In order to apply the plan of controlled solidification to the eutectic to provide the desirable aligned microstructure, solidification along a planar front must be achieved. As hereinafter described in greater detail, theoretical evaluations of the systems of the present invention would suggest that this type of solidification would not be possible in these systems. However, contrary to these theoretical predictions, plane front growth has been effected in various nickel, cobalt and chromium eutectic systems with the Group IV*a* or V*a* monocarbides where the carbide has a high entropy of fusion.

When the high temperature composite of the controlled eutectic is sufficiently resistant to corrosive attack at the anticipated engine service temperatures, the material finds a natural application in the stressed parts of jet engines. An evaluation of the various metallic elements in terms of their respective melting points, mechanical properties, densities and oxidation behavior demonstrates that only a few of these materials are suitable as the matrix material in an alloy designed for services at temperatudes exceeding 1650° F., the more useful materials including nickel, cobalt and chromium.

As the reinforcing medium in these alloys, the carbides, although thermodynamically less stable than oxides, are attractive. The melting points of the carbides are in general the highest of all compositions of matter and carbides can be readily incorporated into the above-mentioned matrix materials by melting techniques, thus avoiding the problems normally associated with the powder metallurgy processes which are normally those employed with the oxides.

The relative thermodynamic stabilities of the carbides are very important, and the standard free energies of formation of a number of carbides are plotted as a function of temperature in FIG. 3. The carbides with the smallest negative free energies of formation have been observed to graphitize in nickel and cobalt. Silicon carbide, for example, graphitizes with nickel, cobalt or chromium, and boron monocarbide graphitizes with either nickel or cobalt. The other monocarbides set forth in FIG. 3, however, are thermodynamically stable in both nickel and cobalt and eutectics exist between these metals and those monocarbides.

Various researchers have classified eutectics according to certain factors including the entropy of melting. From a review of the latent heats of fusion of the carbides and their melting points, specifically niobium carbide, titanium carbide, tantalum carbide and zirconium carbide,

plane front solidification of the metal-monocarbide eutectics would not be expected and, hence, the desired fibrillar structure would appear unattainable. However, notwithstanding the theoretical considerations, plane front growth has been effected in the systems discussed and anisotropic articles have been produced in a number of these systems.

Some of the various systems investigated are set forth in the following table:

TABLE I

System	Vol. percent strengthener	Melting temp., °F.	Tensile strength, p.s.i. (Temp., °F.)
Ni-TiC	5.5	2,390	
Ni-HfC	15–28	2,300	
Ni-NbC	11	2,426	129,000 (75) 25,600 (2,000)
Co-TiC	16	2,480	
Co-HfC	>15		
Co-NbC	12	2,490	1,000,000 (75)
Co-VC	>20		
Cr-CbC	>15		

In the Ni-NbC system, which was selected for an in-depth analysis and to which the very detailed description herein presented is confined for the sake of brevity, a eutectic at about 10 weight percent (13 volume percent) NbC was found at 2422° F., as illustrated in FIG. 4. Master heats of Ni-(0.5–12) weight percent NbC were unidirectionally solidified at rates of from 1–9.8 cm./hr. as set forth in detail in Table II.

TABLE II

System (wt. percent)	Solidification rate (cm./hr.)	Microstructure
Ni-10 NbC	3.0	Partly controlled.
Ni-10 NbC	5.2	Eutectic colonies.
Ni-10 NbC	2.8	Controlled eutectic.
Ni-10 NbC	2.8	Do.
Ni-11 NbC	2.8	Proeutectic NbC.
Ni-11 NbC	2.9	Do.
Ni-12 NbC	2.8	Do.
Ni-12 NbC	2.8	Do.
Ni-0.5 NbC	3.0	Single phase Ni.
Ni-10 NbC	2.9	Controlled eutectic.
Ni-10 NbC	2.8	Do.
Ni-10 NbC	2.8	Do.
Ni-10 NbC	2.8	Do.
Ni-10 NbC	1.9	Controlled eutectic-colonies.
Ni-11 NbC	7.2	Primary NbC.
Ni-11 NbC	6.8	Do.

For Ni-NbC ingots grown in closed end alumina crucibles only those solidified at velocities below 3 cm./hr. were controlled to an aligned microstructure. However, several ingots were produced with a direct water chill block which allowed plane front growth at velocities above those in closed end crucibles.

The intercarbide spacing on an ingot solidified at 3 cm./hr. averaged about 7.3 microns, the spacing decreasing with increasing solidication velocity. It has been found that the mechanical properties of the whisker strengthened alloys were dependent not only upon the volume fraction of strengthener present in the alloy but also upon the interwhisker spacing. In one system analyzed it was found that by decreasing the fiber spacing by a factor of two (through an increase in the solidification velocity) the stress rupture life at 250° C. and 15,000 p.s.i. was increased from less than 4 hours to over 54 hours and the minimum creep rate was decreased by well over two orders of magnitude. A decrease in interfiber spacing results from an increase in the rate of solidification. Hence, the solidification rate should be high. The solidification rate is, however, limited by the tendency of the system to break down from a planar to a cellular liquid-solid interface when the rate is too high. This is due to constitutional supercooling of the liquid directly in front of the solidifying interface caused by a combination of impurity build-up and low thermal gradient in the liquid.

The mechanical properties of a Ni-NbC eutectic specimen directionally solidified at 3 cm./hr. were found to be as follows: ultimate tensile strength 129,000 p.s.i., modulus of elasticity 43×10^6 p.s.i., and a strain at fracture greater than 9 percent.

Assuming the strength of the matrix to be about 35,000 p.s.i. (FIG. 5), the rule of mixtures shows the average stress on the carbide phase to be at least 8.5×10^5 p.s.i., assuming a reasonable elastic modulus of 50×10^6 p.s.i. for the carbide phase.

The rule of mixtures may be expressed as:

$$\sigma_c=V_f\sigma_f+(1-V_f)\sigma_m$$

where:

σ_c is the composite tensile strength;
V_f is the volume fraction of the fibrous phase;
σ_f is the average strength of the fibrous phase; and
σ_m is the strength of the matrix at the failure strain of the composite.

Directionally solidified Ni-NbC eutectic specimens were also tested in tension at elevated temperatures in air, the results of these tests being set forth in FIG. 6. In a comparison with TD nickel, it will be noted that the eutectic material is stronger at all test temperatures. Furthermore, the tensile elongation of the Ni-NbC eutectic is also much greater than that of TD nickel at elevated temperatures.

Stress rupture tests were performed on specimens with an intercarbide spacing of approximately 7.5 microns, the results being presented in FIG. 7.

In the Ni-TiC system a eutectic has been located at about 11.3 weight percent titanium and 0.9 weight percent carbon with ternary eutectics on either side of the pseudo-binary involving graphite at 2320° F. and Ni_3Ti at 2365° F. with TiC and Ni. At the eutectic temperature, the pseudo-binary eutectic consists of a titanium-rich, nickel solid solution matrix and about 5.5 volume percent titanium carbide. Unidirectional solidification at 2.3 cm./hr. was successful, although there was evidence of a decided branching of the fibrous structure. In general, however, the directionally solidified eutectic may be classed as fibrillar despite the more complex geometry. This system does not appear particularly attractive for turbine applications, however, because of the low volume fraction of the dispersed phase, particularly when compared to the Ni-NbC (13 vol. percent) and Ni-HfC (30 vol. percent) systems.

The nickel-hafnium carbide system may be considered pseudo-binary at about 30 weight percent hafnium carbide, but this is a difficult system to employ when utilizing a precombined hafnium carbide powder, partly due to a density segregation and chemisorbed oxygen which makes its solution by the liquid nickel difficult.

In the cobalt-titanium monocarbide systems, the Co-10 wt. percent TiC was found to be eutectic at about 2480° F. Unidirectional solidification of this alloy in alumina crucibles, however, will not be successful due to a metal-ceramic interaction. The Co-HfC system appears to be pseudo-binary at 10 weight percent of the carbide although difficulty was experienced in achieving complete alloying of the hafnium carbide powder with the cobalt.

The Co-NbC eutectic at about 11 weight percent of the carbide was located at 2490° F. An aligned microstructure consisting of rods and platelets was produced by unidirectional solidification at 2.9 cm./hr. Tests on a specimen exhibited whisker reinforcing behavior with a strength of 100,000 p.s.i. and a strain of 0.65%.

The Co-VC eutectic system at about 10 weight percent carbide appears promising since the volume fraction of vanadium carbide exceeds 20 percent. Unidirectional solidification experiments performed at this composition produced primary cobalt. Analysis has revealed that two eutectics may exist in the Co-V-C system, the first and higher melting eutectic being the pseudo-binary section of the ternary between Co and VC at 10 weight percent vanadium and 1.7 weight percent carbon. Extracted whiskers from the binary eutectic region of the ingot were identified as vanadium carbide by X-ray diffraction.

In the solidification of the samples, master castings of the eutectic systems were prepared by induction melting the components under argon cover. Alumina crucibles were used for all the eutectics although beryllia and zirconia would also be suggested, as appropriate. Each ingot was cut into smaller pieces and placed into long, cylindrical-shaped crucibles wherein the eutectics were remelted and unidirectionally solidified under argon by withdrawing the crucible downward from a heat zone produced on occasion either by induction heating or in a resistance-heated graphite furnace.

Tensile testing of the unidirectionally solidified samples was performed on machined specimens oriented such that the loading direction was parallel to the growth direction. The specimens were loaded to failure using a Tinius-Olsen testing machine at a loading rate of 0.01 in./min. at room temperature and a rate of 0.07 in./min. at elevated temperature. Creep rupture behavior was measured in a Satec Model D Creep Rupture Tester under various loads in argon, and elongation was measured from crosshead deflection.

Continuous weight gain measurements on sheet specimens were conducted in oxygen at atmospheric pressure over the temperature range of 700–950° C. using an Ainsworth Thermobalance.

The reinforcement of the nickel, cobalt and chromium matrix materials with the integral aligned monocarbide whiskers according to the present invention affords great promise as the method of replacing the conventional super-alloys in many applications, particularly connected with gas turbine engine operations. The strength of the carbide whiskers in this materials approaches the theoretical failure stress; the system exhibits a composite strain greater than the elastic strain capability of the carbide whiskers; and the microstructure are stable at the elevated temperatures of interest both with respect to the system metallurgy and its chemistry.

While it has been convenient to describe the invention in detail in connection with numerous preferred embodiments and examples, these will be understood to be illustrative only and no limitation is intended thereby. The invention in its true spirit and scope will be measured in accordance with the description set forth in the appended claims.

What is claimed is:

1. An article of manufacture comprising a casting of substantially eutectic composition comprising either nickel, cobalt or chromium alloyed with a carbide selected from the group consisting of the monocarbides of titanium, zirconium, hafnium, vanadium, niobium, and tantalum segregated into a matrix phase consisting essentially of a nickel-base, cobalt-base or chromium-base alloy and a reinforcing phase consisting essentially of said carbide, the reinforcing phase being present predominantly in the form of high strength fibers integrally embedded in the matrix and oriented in a generally parallel spaced relationship.

2. An anisotropic jet engine turbine component comprising a casting of substantially eutectic composition consisting essentially of either nickel, cobalt or chromium and a carbide selected from the group consisting of the monocarbides of titanium, zirconium, hafnium, vanadium, niobium, and tantalum, responsive to unidirectional solidification to yield a reinforcing phase integrally embedded in a matrix phase consisting predominantly of nickel, cobalt or chromium, the reinforcing phase consisting essentially of said carbide in the form of high strength fibers oriented in substantial alignment in the direction of anticipated component tensile loading.

3. A turbine component according to claim 2 in which: the fiber-to-fiber spacing is of the order of less than about 10 microns.

4. A turbine component according to claim 2 wherein: the composition is the nickel-niobium carbide eutectic.

5. A turbine component according to claim 2 wherein: the composition is the cobalt-titanium carbide eutectic.

6. A turbine component according to claim 2 wherein: the composition is the cobalt-vanadium carbide eutectic.

7. A turbine component according to claim 2 wherein: the composition is the chromium-niobium carbide eutectic.

8. The method of forming turbine blade and vane components which comprises the steps of:

providing a eutectic composition consisting essentially of either nickel, cobalt or chromium and a carbide selected from the group consisting of the monocarbides of titanium, zirconium, hafnium, vanadium, niobium, and tantalum;

heating the composition to a temperature above its melting point in an inert atmosphere;

and unidirectionally solidifying the melt in an inert atmosphere at a rate sufficient to establish and maintain planar front solidification, the direction of solidification generally corresponding to the anticipated tensile load axis of the component.

References Cited

UNITED STATES PATENTS

3,098,723	7/1963	Micks	29—183.5
3,124,452	3/1964	Kraft	75—135
3,194,656	7/1965	Vordahl	75—135

RICHARD O. DEAN, Primary Examiner

U.S. Cl. X.R.

75—135, 176