FIG. 1

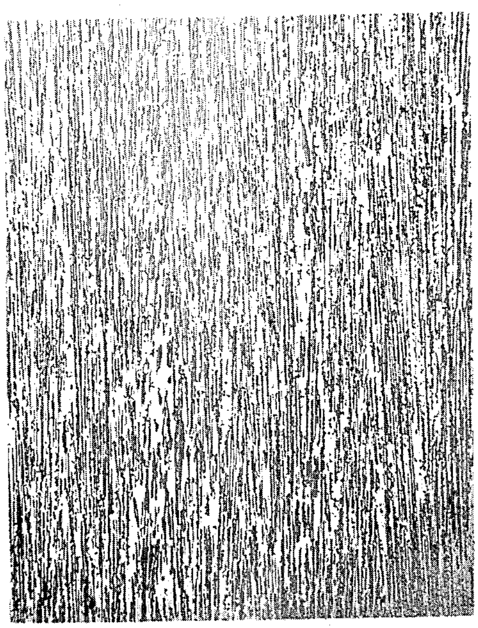

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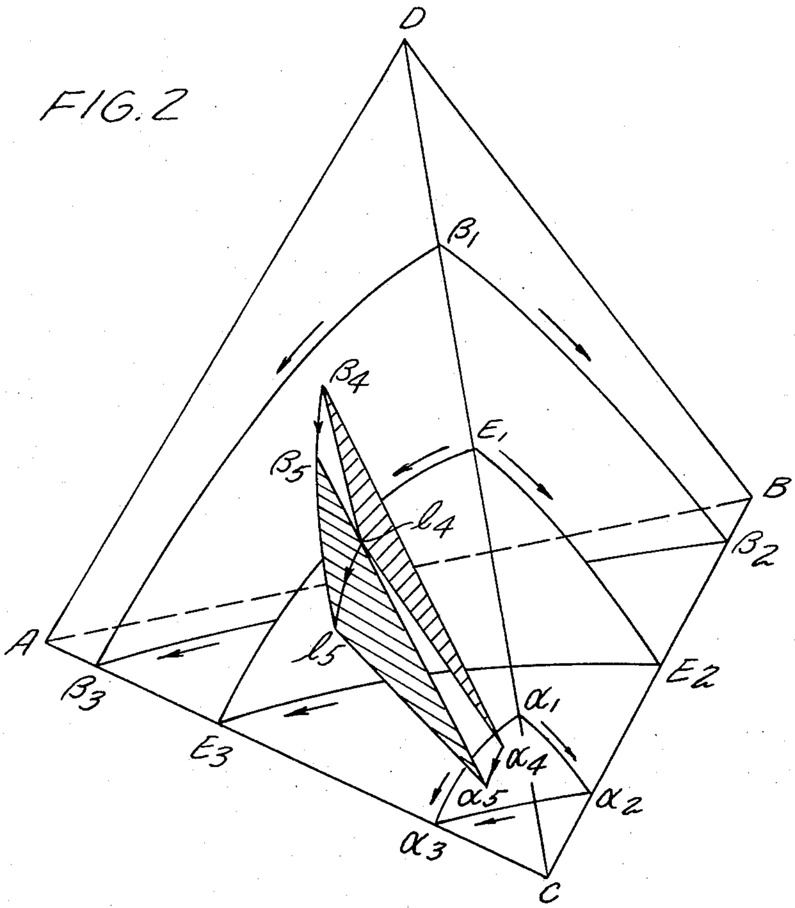
FIG. 2



POLYTHERMAL PROJECTION OF A QUATERNARY ALLOY SYSTEM FREEZING BY THE REACTION $L \rightarrow \alpha + \beta$

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ANISOTROPIC POLYPHASE STRUCTURE OF MULTIVARIANT EUTECTIC COMPOSITION

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ABSTRACT OF THE DISCLOSURE

Quaternary or higher order alloy systems are unidirectionally solidified to provide anisotropic polyphase structures wherein one or more phases of a whisker or lamellar morphology in substantial alignment is embedded in a matrix phase. Included in the systems described are the cobalt, nickel and iron alloys containing chromium, aluminum and/or nickel.

BACKGROUND OF THE INVENTION

The present invention relates in general to those compositions, including the alloys, selected from the quaternary or high order systems which display multivariant eutectic behavior and, more particularly, to such compositions as unidirectionally solidified into polyphase anisotropic structures.

It is known that a number of alloys, such as the binary eutectics, may be directionally solidified from a melt to form an ordered microstructure wherein one phase has solidified in whisker or lamellar form in a matrix of a second phase. A number of eutectics of this nature and the usual techniques to produce in situ whisker strengthening are described in the patent to Kraft 3,124,452 which shares a common assignee with the present invention.

A recognized disadvantage to the usual binary eutectic or pseudo-binary eutectic approach in the production of composite structures by directional solidification techniques has been the lack of versatility of these systems for many applications. For a given material at the eutectic composition, the volume fraction and chemistry of the respective phases are fixed by the uniqueness of the invariant equilibrium. Accordingly, since no significant variation in the volume fraction or chemistry of the phases is possible during equilibrium freezing, the total number of these alloys having all of the requisite characteristics or optimum properties for a specific, predetermined use is very limited, particularly when several different physical or chemical criteria are demanded for that use.

In a copending application entitled "Anisotropic Polyphase Structure of Monovariant Eutectic Composition" by the present inventors, application Ser. No. 734,821, now Pat. No. 3,564,940, assigned to the present assignee, there were described as a series of structures formed from those compositions solidifying over a temperature and composition range according to the monovariant eutectic reaction. In the systems displaying monovariant eutectic behavior, the number of solids forming from a melt are $n-1$, where n is the number of components in the system.

The monovariant eutectic systems, of course, provide a considerable measure of latitude in the selection of

compositions satisfying particular end objectives, particularly when compared to the invariant eutectic compositions. Thus, in the monovariant system there exists a unique capability of changing the chemistry and morphology of the phases, along the eutectic trough of their phase diagram, and it is possible to alter the volume fractions of their phases as well as their compositions.

SUMMARY OF THE INVENTION

This invention relates to aligned polyphase structures formed from the quaternary or high order compositions which respond to unidirectional solidification from a melt to form a dispersed fibrous or lamellar phase or phases embedded in substantial alignment in a matrix phase. In particular, the structures contemplated are formed from the compositions which are multivariant thermodynamically and not as in the binary systems invariant at a fixed composition or as the monovariant eutectic systems variant monolinearly along a eutectic trough.

In a preferred embodiment, compositions formed as described herein consist of an aligned fibrous or lamellar, collectively referred to as fibrous, phase or phases embedded in a cobalt, nickel or iron solid solution matrix phase.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a photomicrograph of a quaternary cobalt-base alloy containing nickel, chromium and carbon, unidirectionally solidified at a rate of 10 cm./hr. to provide an aligned microstructure.

FIG. 2 is a phase diagram comprising a polythermal projection of a quaternary system illustrating freezing of an alloy by the reaction $L \rightarrow \alpha + \beta$.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The processing by which the phase alignment is achieved is similar to that used for the invariant and monovariant eutectics, and is involved with the simultaneous freezing of two or more solid phases from the liquid. Thus, the preparation techniques described by Kraft, supra, and others, with the solidification parameters selected to provide macroscopically plane front growth, successful solidification rates generally being achieved within at least the range of 2–20 cm./hr.

The basic example involved here is for the sake of convenience and ease of graphical illustration described and defined principally with respect to a quaternary alloy system, although it is applicable to and has been demonstrated with higher order systems as well. For a quaternary, the reaction which produces the desired anisotropic polyphase structures is that of separation of two solids from the liquid. FIG. 2 shows a polythermal projection of a simple, hypothetical quaternary system, ABCD, where A, B, C and D are the system components. The binaries AC, BC and CD form the eutectics E_1, E_2 and E_3, respectively, and the corresponding melting temperature are on the order $E_1 > E_2 > E_3$. The systems between A, B and D form a continuous series of solid solutions. The faces of the tetrahedron show polythermal projections of the ternary systems ACD, ABC, and BCD. No reactions are shown on the ABD face of the tetrahedron since this is on isomorphous system.

For normal behavior the binary eutectics E_1, E_2, and E_3 solidify upon directional casting to form anisotropic structures as taught by Kraft, supra, at a fixed composition and temperature. Similarly, the lines E_1E_2, E_1E_3, and E_2E_3 define monovariant eutectic troughs, and compositions lying along these lines, excluding the end points, may be solidified by directional casting techniques to produce anisotropic polyphase structures, as taught in the copending application relating to monovariant eutectic systems.

The surface $E_1E_2E_3$ (liquidus surface), excluding the end lines and end points, is, in the system described, the locus of those compositions covered herein. An alloy on this surface, of composition l_4, begins to freeze forming solids α_4 and β_4 simultaneously. The composition of the liquid shifts along the line l_4l_5 while the equilibrium compositions of the crystallizing solids shift along the lines $\alpha_4\alpha_5$ and $\beta_4\beta_5$. At l_5 the last liquid freezes with α_5 and β_5 as the conjugate solids. Thus, the process which has been traced is one involving the simultaneous formation of two solids from the melt via the non-isothermal reaction $L=\alpha+\beta$.

In terms of the phase rule, at a fixed pressure two independent variables must be selected for the quaternary to define the state of the system. Concentration of two of the components, or one of the components and a temperature, may be used to map the liquidus surface. In a quinary system three independent variables for the reactions $L=\alpha+\beta$ describe a liquidus volume while the non-isothermal reaction of the type $L=\alpha+\beta+\gamma$ would be located on the liquidus surface. Thus, as used herein, the compositions solidifying according to the multivariant eutectic reaction are those defined by the liquidus surface (quaternary systems) or liquidus volume (higher order systems), exclusive in the case of the quaternary systems, of boundary compositions.

The ability to form an anisotropic biphase structure employing the teachings herein was demonstrated in the cobalt-chromium-nickel-carbon quaternary. An alloy of the nominal composition, by weight, 41 percent chromium, 10 percent nickel, 2.4 percent carbon, balance cobalt was unidirectionally solidified at approximately 10 cm./hr. Growth occurred by macroscopically plane front solidification to provide an aligned microstructure, as evidenced by FIG. 1. The structure comprises a matrix phase consisting essentially of cobalt, chromium nickel and carbon in solid solution and a reinforcing phase comprising on M_7C_3 type of carbide, when M consists of chromium, cobalt and nickel. Alloys having nominal compositions of, by weight, 41 percent chromium, 2.4 percent carbon, 1.5 percent aluminum, balance cobalt; and 41 percent chromium, 10 percent nickel, 2.4 percent carbon, 1.5 percent aluminum, balance cobalt; have also been subjected to directional solidification to establish suitability for application to the formation of multiphase composite microstructures according to the multivariant eutectic reaction.

An iron-base alloy of the nominal composition, by weight, 43 percent iron, 35 percent chromium, 20 percent nickel and 2 percent carbon, as directionally solidified at 8 cm./hr. provided an aligned microstructure with the aligned phase comprising the carbide Cr_7C_3 embedded in a solid solution matrix of iron, nickel and chromium. Similarly, phase alignment according to the multivariant eutectic reaction has been demonstrated in the nickel-base alloy systems including an alloy of the composition, by weight, 36 percent chromium, 10 percent cobalt, 1.5 percent carbon, balance essentially nickel.

Fiber-strengthened composite structures may be particularly attractive for gas turbine engine use when the melting points of the respective phases are high and the reinforcing phases are strong. With the present invention considerable compositional latitude is provided to afford

not only reasonable high temperature strengths but also a balance of other alloy criteria such as oxidation, sulfidation, erosion and thermal shock resistance. And, of course, since the mechanisms involved in the generation of these composites is one of equilibrium freezing, there is provided, in general, good metallurgical and chemical stability over the temperature ranges contemplated in practical use.

While the present invention has been described in detail with reference to specific examples for the purpose of illustration, the invention in its broader aspects is not limited to the specific details described, for obvious modifications will occur to those skilled in the art.

What is claimed is:

1. A unidirectionally solidified anisotropic body formed of the quaternary or higher order material systems of multivariant eutectic composition segregated into a matrix phase and at least one dispersed phase, said dispersed phases being fibrous with the individual fibers thereof oriented in substantial alignment over a substantial portion of the body and embedded in the matrix phase.

2. The body of claim **1** wherein the matrix phase consists of a cobalt, nickel or iron-base alloy.

3. A unidirectionally solidified anisotropic body formed of the quaternary or higher order alloys of multivariant eutectic composition segregated into a matrix phase consisting essentially of a nickel-cobalt or iron-base alloy and a dispersed phase, the dispersed phase consisting of a plurality of high strength carbide fibers oriented in substantial alignment over a substantial portion of the body and integrally embedded in the matrix phase.

4. A unidirectionally solidified anisotropic composite formed of the quaternary or higher order alloys of multivariant eutectic composition which comprises a matrix phase consisting of an alloy of cobalt, nickel or iron, and a dispersed phase embedded therein in the form of high strength fibers oriented in substantial alignment over a major portion of the composite, the dispersed phase consisting essentially of a carbide of the M_7C_3 type, where M is either chromium or a mixture of elements including chromium.

5. A unidirectionally solidified article formed of the quaternary or higher order alloys of multivariant eutectic composition having anisotropic properties comprising a fiber-strengthened composite consisting of a cobalt alloy matrix and an aligned fibrous phase consisting of a mixed carbide of the M_7C_3 type where M includes chromium and cobalt.

6. A unidirectionally solidified article formed of the quaternary or higher order alloys of multivariant eutectic composition having anisotropic properties comprising a fiber-strengthened composite consisting of a nickel alloy matrix and an aligned fibrous phase consisting of a mixed carbide of the M_7C_3 type where M includes chromium and nickel.

7. A unidirectionally solidified article formed of the quaternary or higher order alloys of multivariant eutectic composition having anisotropic properties comprising a fiber-strengthened composite consisting of an iron alloy matrix and an aligned fibrous phase consisting of a mixed carbide of the M_7C_3 type where M includes chromium and iron.

8. As an article of manufacture, a unidirectionally solidified casting of a nominal composition consisting essentially of, by weight, about 41 percent chromium, about, 2.4 percent carbon, remainder cobalt together with at least one of the following, about 10 percent nickel, about 1.5 percent aluminum, the casting being characterized by pronounced alignment of a dispersed phase comprising a carbide of the M_7C_3 type, where M is predominantly chromium.

9. As an article of manufacture, a unidirectionally solidified casting of a nominal composition consisting essentially of, by weight, about 36 percent chromium, 10 percent cobalt, 1.5 percent carbon, balance nickel, the casting being characterized by pronounced alignment of a dispersed phase comprising a carbide of the M_7C_3 type, where M is predominantly chromium.

10. As an article of manufacture, a unidirectionally solidified casting of a nominal composition consisting essentially of, by weight, about 35 percent chromium, 20 percent nickel, 2 percent carbon, balance iron, the casting being characterized by pronounced alignment of a dispersed phase comprising a carbide of the M_7C_3 type, where M is predominantly chromium.

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75—134 N, 134 F, 135, 171; 148—31, 32