

March 25, 1969

F. D. LEMKEY

3,434,827

ANISOTROPIC MONOTECTIC ALLOYS AND PROCESS FOR MAKING THE SAME

Filed July 16, 1965

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FIG. 1

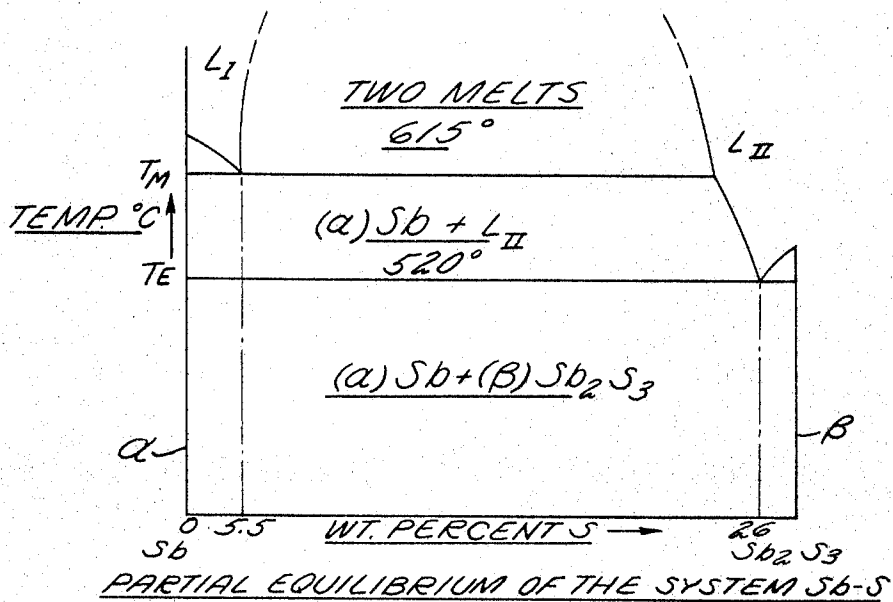
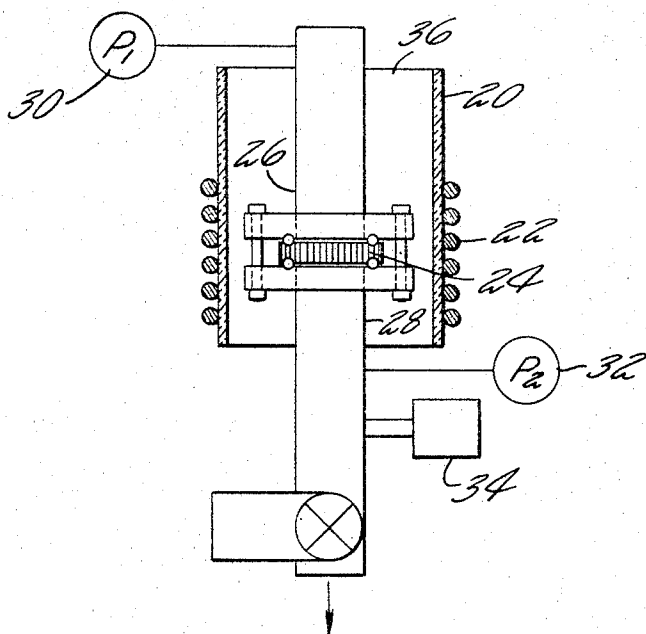


FIG. 8



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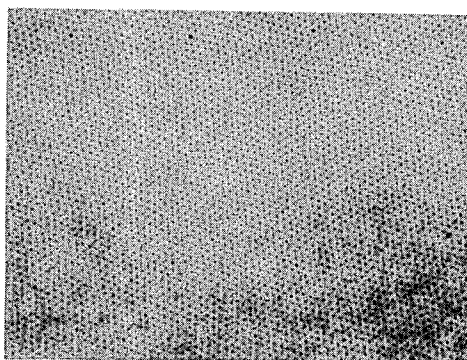


FIG. 2

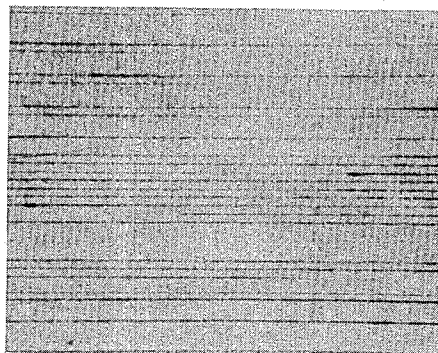


FIG. 3

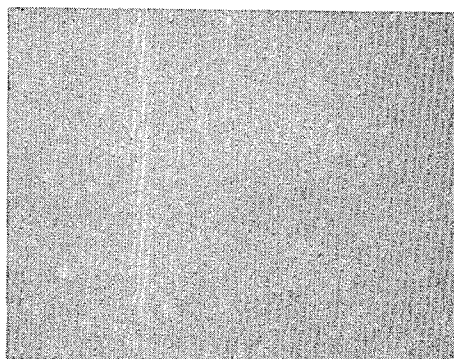


FIG. 4

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FIG. 7

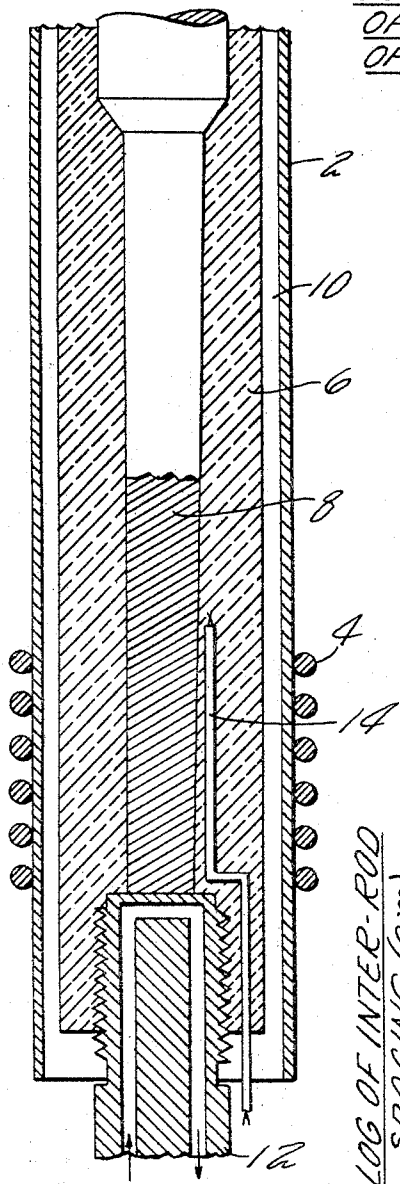


FIG. 5
SCHEMATIC REPRESENTATION
OF STEADY STATE GROWTH
OF A ROD-LIKE MONOTECTIC

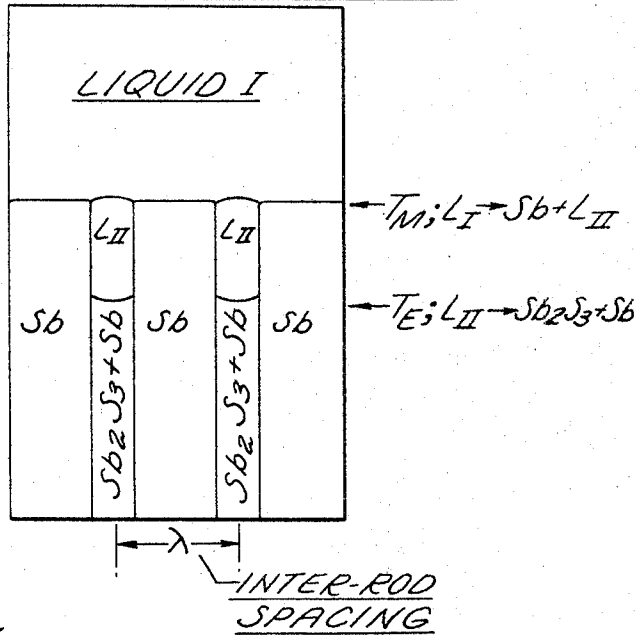
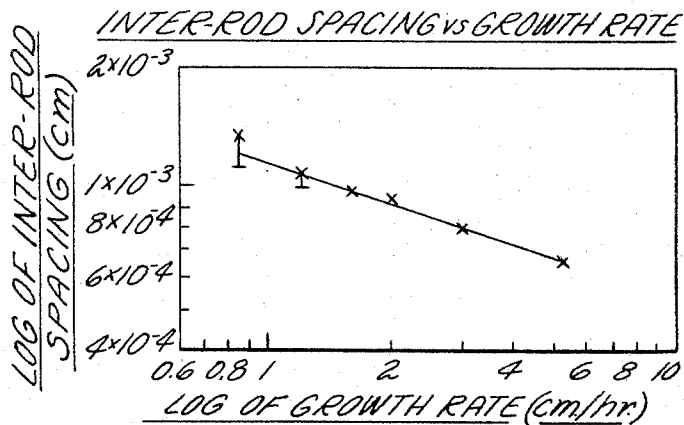


FIG. 6



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ANISOTROPIC MONOTECTIC ALLOYS AND PROCESS FOR MAKING THE SAME

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14 Claims

ABSTRACT OF THE DISCLOSURE

Monotectic compositions are solidified to form a body wherein one of the products of solidification forms as filaments embedded in a matrix of a second product of solidification, the filaments being arranged in parallel, spaced relationship and having a melting point lower than that of the matrix material. Because of the difference in melting points of the two products of solidification, the body may be reheated to a temperature at which the filaments melt while the matrix remains solid. The molten material may then be selectively removed to form a body with uniaxial porosity or other useful properties.

This invention relates in general to unidirectionally-solidified alloys and compositions characterized by a high degree of microstructural regularity and continuity, and to methods for producing such alloys. More particularly, this invention contemplates the formation of anisotropic alloy compositions from monotectic alloys wherein the lower melting product of solidification forms as rods or filaments embedded in a higher melting solidification product. It further contemplates the production of porous matrix materials from the unidirectionally solidified ingot, the pores of which are of uniform size and shape and are substantially straight, independent and parallel with respect to one another.

It is known that certain polyphase alloys having microstructures which consist predominantly of very fine, three dimensional lamellae oriented substantially parallel to a common direction may be produced by unidirectional solidification techniques. These microstructures are generally formed from a eutectic composition or alloy, as discussed in the patent to Kraft, 3,124,452, a eutectic composition being defined as one in which two or more types of crystals freeze simultaneously at a fixed temperature, called the eutectic temperature, upon cooling from the liquid state. In those eutectic compositions which can be caused to grow in the form of three-dimensional lamellae, when one of the phases in a two phase alloy is caused to grow as parallel rod-like lamellae throughout a large specimen, the other phase will form a matrix in which the rods are embedded.

It is an object of the present invention to produce alloys having a microstructure which consists predominantly of a rod-like product of solidification embedded in a matrix product, the two products being characterized by different physical properties including different melting points.

It is a further object of this invention to produce alloys having a microstructure in which the rod-like material is regularly and uniformly distributed in an ordered relationship within the body of the matrix.

An additional object is the provision of anisotropic alloy compositions in which the rod-like material is in the form of filaments of uniform configuration, size and orientation, each filament being structurally independent of each other filament over a substantial length.

Another object is to provide a method of producing porous matrix materials from such alloys, the pores comprising a plurality of uniform, parallel and independent

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channels of substantial length regularly spaced throughout the matrix.

These and other objects and advantages of this invention will be evident from the following description or from practice of this invention as taught herein.

It has been demonstrated that by the monotectic reaction, in which one liquid phase (L_I) decomposes with decreasing temperature into a solid phase (α) and a new liquid phase (L_{II}), compositions can be unidirectionally solidified to yield microstructures in which the products of solidification of the L_{II} phase are present in the form of uniformly thin rods, all of which are essentially parallel and regularly spaced over considerable distances. Since the L_{II} phase freezes at a lower temperature (T_E) than that of the matrix (α phase), it is possible to reheat the solidified structure above the freezing temperature of the rods and form liquid channels within the matrix. The liquid may then be forced out of the channels by imposing a suitable pressure differential across the channels in a direction parallel to their longitudinal axes.

The present invention may best be described by reference to the following drawings, in which:

FIGURE 1 is a partial equilibrium diagram of the system Sb-S which undergoes the monotectic reaction.

FIGURE 2 is a photomicrograph of a section of the unidirectionally solidified structure of the monotectic system Sb-S taken normal to the rod axis.

FIGURE 3 is a photomicrograph of the monotectic system Sb-S taken parallel to the axis of the rods.

FIGURE 4 is an enlarged photomicrograph of the Sn-S monotectic system illustrating the uniformity of rod configuration and spacing in the material.

FIGURE 5 is a schematic representation of the steady-state growth of a rod-like monotectic.

FIGURE 6 is a diagram illustrating the effect of the rod growth rate on the inter-rod spacing.

FIGURE 7 is a sketch of the solidification apparatus used in the formation of the materials of the present invention.

FIGURE 8 is a schematic of a liquid blower usable in the formation of porous matrices according to this invention.

The monotectic reaction has much in common with the eutectic reaction involving the simultaneous production of two or more phases in fine states of subdivision. Freezing proceeds by nucleation and subsequent growth and it is difficult to distinguish between these two stages from the microstructures of the as-cast monotectic alloys.

In the Sb-S system to which most of the discussion will be directed for the sake of brevity, the monotectic invariant occurs at 1.5 weight percent (5.5 atomic percent) sulfur. The phase diagram indicating the equilibria involved is illustrated in FIGURE 1. When phase L_I , rich in antimony, is cooled through the three phase reaction isotherm (615°C.), solid antimony and phase L_{II} , a liquid rich in sulfur, simultaneously appear. Upon further cooling to a temperature of 520°C. , phase L_{II} undergoes a eutectic reaction in which Sb_2S_3 and antimony are simultaneously crystallized.

The postulated crystal growth yielding the rod-like structure adjacent the solid-liquid interface in the Sb-S system upon controlled solidification is illustrated schematically in FIGURE 5. As illustrated, the matrix is antimony and the rod-like structure is the Sb_2S_3 -Sb eutectic. It is theorized that two liquid-solid interfaces advance as solidification proceeds, one at an axial position in the solidification apparatus whereat the temperature corresponds to the monotectic isotherm (T_M) and the other whereat the temperature corresponds to the eutectic isotherm (T_E).

It has been discovered that most monotectics investigated do not entrap the liquid formed (L_{II}) at the mono-

tectics isotherms as in the case with the above-described Sb-S system, but instead the leading liquid-solid advances the phase L_{II} and it eventually solidifies at the grain boundaries. Others have investigated the interaction between the liquid particles and the solid-liquid interface and have found that, for a given type of particle, solid or liquid, there exists a critical interface propagation rate below which particles may be rejected or pushed aside and above which they are entrapped. No such critical velocity has been found in connection with the Sb-S system, however.

In the controlled monotectic specimens studied it has been observed that both phases extend in a direction very nearly parallel to that corresponding to the direction of solidification. However, when a perturbation is introduced into an otherwise steady structural growth rate during the unidirectional solidification, these perturbations are reflected as banding on the structure and trace the position of the macroscopic liquid-solid interface which is slightly convex in some cases toward the liquid.

Although there are in excess of 250 monotectic systems reported in the literature, it has been noted that most monotectics do not entrap liquid at the monotectic isotherm. While, for the sake of brevity, most of the detailed description concerning the present invention has been generally directed to the antimony-sulfur monotectic system, there are other monotectic systems which may be used to form the products of the present invention, and examples of such systems are cited for illustrative purposes in Table 1. However, it will be understood that this listing is not intended to be exclusive.

TABLE 1

No.	Alloy System	Matrix	Rod Structure
1.....	Sn-S.....	SnS.....	Sn-SnS
2.....	Cu-S.....	CuS ₂	Cu-Cu ₂ S
3.....	Ag-S.....	Ag.....	Ag ₂ S-Ag
4.....	In-S.....	InS.....	In-InS
5.....	Tl-S.....	Tl ₂ S.....	Tl-TlS

The quantitative variation of interphase spacing as a function of solidification rate is illustrated in FIGURE 6 and was studied by measuring the inter-rod distances between the nearest neighbors in a plane perpendicular to the rod axis. The data accumulated indicates that radial solute diffusion in the liquid ahead of the advancing interface plays an important role in controlling the inter-rod spacing.

It has similarly been established that an increase in the rate of the planar solid-liquid interface movement decreases both the spacing and the diameter of the rods. Therefore, by judicious selection of the interface propagation rate the number of filaments per unit area may be varied. Similarly, by means of intermediate changes in the solidification velocity matrices containing filaments whose diameter varies with their length may be produced, and additionally, by selectively removing the aligned phase or phases, matrices exhibiting multiple porosity may be achieved.

Although the mechanism of this invention is described with specific reference to the true monotectic compositions of the various alloys, it is possible to produce the structures described with considerable deviation from the true monotectic composition. When such a deviation is permitted, the product will usually still be characterized by the desired ordered filamentary microstructure. However, the product will also be characterized by the presence of relatively larger crystals of one of the elements or alloys selectively distributed throughout the microstructure. These are normally referred to as primary crystals since they are the first crystals to solidify as the temperature of the melt is lowered in the solidification process. This mechanism is well understood by those conversant in the art.

It is also contemplated that minor additions of specific impurities may be advantageously made to the melt prior

to the controlled solidification to impart specific properties to either the matrix structure or the filamentary material or to further enhance properties otherwise inherent therein. For example, an intentionally added impurity which exhibits solid solubility with the matrix material may be utilized to alter the electrical properties of the matrix to achieve a specific electrical resistivity, or to alter its magnetic properties.

Throughout this description and in the claims which follow, it has been convenient to describe the lower melting product of solidification in the unidirectionally solidified ingot as rod-like, rods or filaments. However, it will be evident that the cross-sectional shape of the individual filaments is not critical. The filaments need not be circular in cross-section nor is it necessary that the ingot or rods be in the form of a straight cylinder. Nor is it necessary that the length of the rod exceed its diameter although such will normally be the case. The terms rods and filaments then will be understood to include a wide variety of solidification product configurations in the context as herein intended.

Alloy specimens were prepared by mixing the individual components in a quantity approximately corresponding to the monotectic composition. The mixture was sealed in an evacuated quartz tube and the tube was heated to and held at a temperature of approximately 450° C. (in the case of the Sb-S system) for 24 hours before any controlled solidification was undertaken. It will be understood, of course, that in this or other systems different temperatures and different reaction times will be satisfactory or necessary, depending upon the physical and chemical characteristics of the elements involved and the equipment utilized. The precise parameters specified for the reaction step are relatively immaterial as long as they are sufficient to effect the desired reaction between the individual components. It should be emphasized, however, that considerable care must be exercised during the reaction process for safety reasons, particularly when the individual components are characterized by widely divergent melting and boiling points. In the Sb-S system for example, the sulfur melts at about 119° C. and boils at 445° C. while the antimony melts at 630° C. During the process of reacting these two elements, therefore, it will be seen necessary that due consideration be given to the potential pressure buildup in the reaction vessel due to vaporization of the sulfur as the temperature is increased. In the Sb-S system, the reaction temperature was selected to yield a slightly superheated liquid sulfur and yet to permit the use of conventional glassware reaction equipment. The selection of the parameters necessary to react the various components when other materials are utilized is well within the knowledge of those skilled in the art.

It is, of course, possible to effect the requisite reaction between components directly in the crucible of the solidification apparatus discussed below. However, because the speed of the reaction is determined, at least in part, by the developed area at the interface between the liquid sulfur and the solid antimony the reaction was normally effected in a separate step with the axis of the finished specimen oriented in a generally horizontal direction to provide for the desired increased contact area between solid and liquid.

After the reaction went to completion, the specimen was removed from the quartz tube and vertically positioned within a unidirectional solidification furnace of the form illustrated schematically in FIGURE 7. This apparatus comprises a hollow containment tube 2 partially surrounded by an induction coil 4 which is suitably attached to a power source, not shown. Slidably mounted within the containment tube 2 is a graphite crucible 6 wherein the specimen 8 is positioned, the annular space 10 surrounding the crucible normally being filled with argon or some other protective atmosphere to protect the crucible and from atmospheric contamination during

the heating process. The crucible 6 is counterbored at its lower end and threaded to a water-cooled brass plug 12, the plug being attached to a variable drive mechanism (not shown) whereby the crucible may be drawn down through the induction coil at a predetermined rate. Thermocouple 14, shown projecting upwardly through the bottom of the crucible cavity wherein the specimen is carried, is used to sense the temperature of the specimen and establish that the specimen is completely liquified before withdrawal of the crucible from the furnace and directional solidification is commenced.

After the crucible had been positioned in the crucible cavity, power was applied to the induction coil and the temperature of the specimen was raised to a temperature in excess of the monotectic isotherm. Preferably the entire specimen is melted before a resolidification is attempted, although it was quite common in the tests conducted to initiate the process with a small portion of the specimen remaining unreacted where is abutted the water-cooled brass plug 12. When the specimen had been completely melted, cooling water was admitted to the brass plug and unidirectional solidification was effected by slowly withdrawing the crucible from the furnace.

The freezing rate over the central portion of the ingot was varied generally from 0.8 to 8.0 cm./hr., this range being defined by the physical limitations of the equipment being utilized. The imposed temperature gradient in the liquid was approximately 70° C./in. in the vicinity of the monotectic reaction, and the ingots were unidirectionally solidified usually to a length of approximately 5 inches, although this length was a purely arbitrary selection. The temperature gradient will be understood to mean the change in temperature in the liquid per inch of length in the liquid immediately in front of the advancing solid monotectic interface. In every ingot fabricated a fine-grained structure was produced at the end of the specimen which was first crystallized and from this polycrystalline region evolved the large grains elongated in the direction of growth.

While it is preferred to both completely liquefy the monotectic specimen prior to resolidification and further to initiate the solidification at the bottom of the specimen, this recommended technique is not necessary as long as a stable solid-liquid interface is established and a predetermined grain growth rate program is maintained. Similarly, although the solidification was undertaken with the apparatus mounted vertically, equally good results will be obtained in modified equipment oriented in directions other than the vertical.

As has been previously noted and discussed in connection with FIGURES 2, 3 and 4, the solidified product is characterized by a high degree of microstructural regularity and continuity. The structure consists of a plurality of rods or filaments of consistent cross-sectional area and configuration regularly disposed in a matrix material of a different composition. Further, the rods are all parallel and independent substantially throughout the length of the matrix structure. It will be further noted from the various systems, cited for illustrative purposes in Table 1, that through the practice of this invention it is possible to form a structure wherein the rods are electrically conductive and the matrix is semi-conductive or, conversely, to produce a structure wherein the rods are semi-conductors emmeded in a conductive matrix material. For example, in the Sb-S system of FIGURE 2 and 3, the matrix is antimony and, accordingly, an electrical conductor. On the other hand, in the Sn-S system of FIGURE 4, the matrix is tin sulfide, a semi-conductor. The usefulness of the products of this invention in the electrical and electronic industries will be obvious.

It is further suggested that through the practice of this invention by selectively dissolving the matrix material from the periphery of the rods in the solidified

ingot, it is possible to produce very thin fibers of essentially uniform cross section and length.

Since a structure is produced wherein the rod-like material has a lower melting point (T_E) than the matrix material (T_M), it is possible to reheat the specimen to a temperature intermediate the two melting points and from liquid channels within the solid matrix. The liquid may be forced out of the channels by applying a suitable pressure differential across the specimen in a direction parallel to the channels sufficient to overcome the surface tension of the liquid. Once the critical pressure differential has been established for breakaway and the liquid removed, the flow of gas through the specimen together with the pressure drop will define the efficiency of the liquid removal, the flow rate being related to the pressure drop across the specimen and the number of open channels for Hagen-Poiseville flow. In this manner it is possible therefore to form a plate which is characterized by relatively uniform and unidirectional porosity. Further, in addition to the use of articles formed in this manner as porous materials, these structures may have other elements or materials with favorable melting points and surface tensions backfilled into the channels, yielding articles of potentially useful and unique properties. A particularly useful example of this type would comprise a refractory matrix with a uniformly dispersed low melting phase backfilled into the pores, resulting in a structure which will ablate uniformly in one direction in a high temperature environment.

A schematic of liquid blower illustrated in FIGURE 8 has been utilized to demonstrate the removal of liquid from the channels in thin discs cut from unidirectionally solidified ingots. The blower comprises a quartz envelope 20 surrounded by an induction heating coil 22. The specimen 24 is suitably positioned within the quartz envelope internal of the induction coils and between two flanged conduits 26 and 28 through which high pressure inert gas is circulated. A pressure gage 30 communicating with the flow passage within the conduit 26 and a second pressure gage 32 communicating with the flow passage within conduit 28 are utilized to establish the appropriate pressure differential across the specimen. A flowmeter 34 is provided to sense the flow rate of inert gas within the conduit 28. The selection of appropriate materials usable in this apparatus is within the state of the art and a quartz envelope surrounding conduit materials composed of stainless steel have been utilized. It may be found advantageous to circulate an inert gas such as argon in the annulus 36 formed between the envelope and the conduits to prevent oxidation of the conduit material and contamination of the specimen at the processing temperatures.

Although the use of a gas pressure differential has been suggested as a possible means of preferentially removing the rod-like material from the solidified structure to form pores therein, it will be understood that other means are contemplated. For example, in a given system, the obvious difference in vapor pressures between the individual products of solidification may suggest that a controlled ablation or evaporation technique may advantageously be utilized. Further, depending again on the chemical nature of the system involved, it may be preferable to selectively dissolve the rod material and form the porous structure in this manner.

I claim:

1. An antimony-sulfur monotectic composition characterized by a microstructure which comprises a matrix consisting essentially of antimony and a plurality of substantially uniform and parallel filaments embedded in said matrix in uniform array, said filaments consisting essentially of an antimony-antimony trisulfide eutectic.

2. A tin-sulfur monotectic composition characterized by a microstructure which comprises a matrix consisting essentially of stannous sulfide and a plurality of substantially uniform and parallel filaments embedded in said

matrix in uniform array, said filaments consisting essentially of tin-stannous sulfide eutectic.

3. A silver-sulfur monotectic composition characterized by a microstructure which comprises a matrix consisting essentially of silver and a plurality of substantially uniform and parallel filaments embedded in said matrix in uniform array, said filaments consisting essentially of a silver-silver sulfide eutectic.

4. A copper-sulfur monotectic composition characterized by a microstructure which comprises a matrix consisting essentially of cuprous sulfide and a plurality of substantially uniform and parallel filaments embedded in said matrix in uniform array, said filaments consisting essentially of a copper-cuprous sulfide eutectic.

5. An article of manufacture characterized by uniaxial porosity formed from that class of monotectics in which one of the products of solidification forms as filaments embedded in a second product of solidification, said filaments having a lower melting point than said second product of solidification, comprising a matrix consisting of said second product of solidification having uniformly disposed therein a plurality of substantially straight, independent and parallel channels, said channels having a relatively uniform size and configuration and being formed by the selective removal of said filaments.

6. An anisotropic body formed from that class of monotectics in which one of the products of solidification forms as filaments embedded in a second product of solidification, said filaments having a lower melting point than said second product of solidification, comprising a matrix consisting of said second product of solidification having uniformly disposed therein a plurality of substantially straight, independent and parallel channels, said channels having a relatively uniform size and configuration and being formed by the selective removal of said filaments, and a third material backfilled into said channels, said third material having a melting point lower than said second product of solidification.

7. The method of forming anisotropic alloy compositions comprising the steps of:

forming a monotectic composition selected from that group of monotectics in which one of the products of solidification forms as filaments embedded in a second product of solidification, the filaments being substantially uniform in size and regularly spaced in parallel relationship over a substantial length, heating the composition to a temperature above the monotectic temperature, and unidirectionally solidifying the melt to cause filament growth.

8. The method of claim 7 wherein: the monotectic composition is selected from that group of monotectic systems consisting of Sb-S, Sn-S, Ag-S, Cu-S, In-S and Ti-S.

9. The method of forming a body of uniaxial porosity comprising the steps of:

forming a monotectic composition selected from that group of monotectics in which one of the products of solidification forms as filaments embedded in a second product of solidification, said filaments being substantially uniform in size and regularly spaced in parallel relationship over a substantial length, heating the composition to a temperature above the monotectic temperature,

unidirectionally solidifying the melt to cause filament growth, and selectively removing the filament material to form a porous body.

10. The method of claim 9 wherein: the monotectic composition is selected from that group of monotectic systems consisting of Sb-S, Sn-S, Ag-S, Cu-S, In-S and Ti-S.

11. The method of claim 10 wherein the selective removal of the filament material includes the steps of: reheating the body to a temperature intermediate the melting points of the first and second products of solidification whereby the filaments are liquefied, and imposing a pressure differential across said body sufficient to eject the liquefied filament material.

12. The method of claim 10 wherein the selective removal of the filament material includes the steps of: reheating the body to a temperature intermediate the melting points of the first and second products of solidification whereby the filaments are liquefied, and imposing a vacuum on the body whereby the filament material is selectively evaporated.

13. The method of forming articles having anisotropic properties comprising the steps of:

forming a monotectic composition selected from that group of monotectics in which one of the products of solidification forms a filament embedded in a second product of solidification, said filaments being substantially uniform in size and regularly spaced over a substantial length,

heating the composition to a temperature above the monotectic temperature, unidirectionally solidifying the melt to cause filament growth,

selectively removing the filament material to form a porous body, and

backfilling the porous of the porous body with a third material having a melting point below that of the second product of solidification.

14. The method of forming fibers of uniform shape, diameter and length comprising the steps of:

forming a monotectic composition from that group of monotectics in which one of the products of solidification forms as filaments embedded in a second product of solidification, said filaments being substantially uniform in size and regularly spaced in parallel relationship over a substantial length, heating the composition to a temperature above the monotectic temperature, unidirectionally solidifying the melt to cause filament growth, and

selectively removing the second product of solidification to release the individual filaments.

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RICHARD O. DEAN, *Primary Examiner*.

U.S. Cl. X.R.

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