

Sept. 7, 1965

M. B. VORDAHL

3,205,099

STABLE DISPERSOID COMPOSITES AND PRODUCTION THEREOF

Filed June 14, 1961

2 Sheets-Sheet 1

Fig. 1.

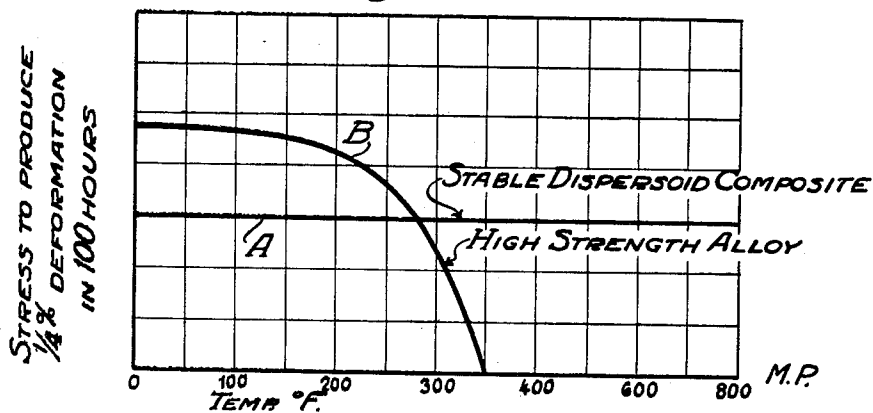


Fig. 3.

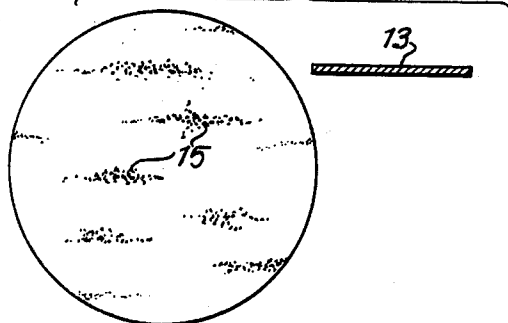


Fig. 2.

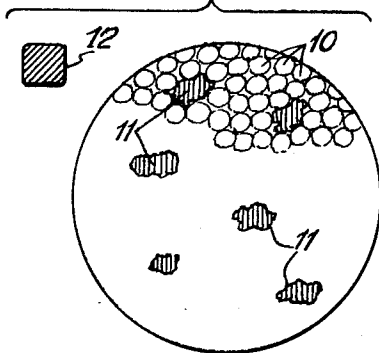
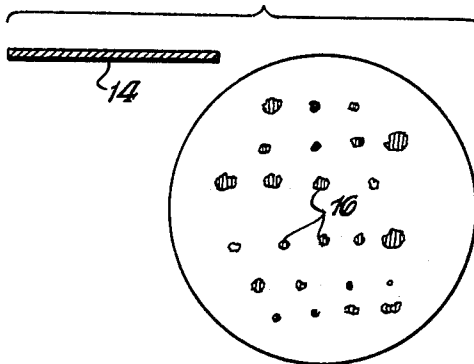


Fig. 4.



INVENTOR.
MILTON B. VORDAHL
BY

John R. Egan
ATTORNEY

Sept. 7, 1965

M. B. VORDAHL

3,205,099

STABLE DISPERSOID COMPOSITES AND PRODUCTION THEREOF

Filed June 14, 1961

2 Sheets-Sheet 2

Fig. 5.

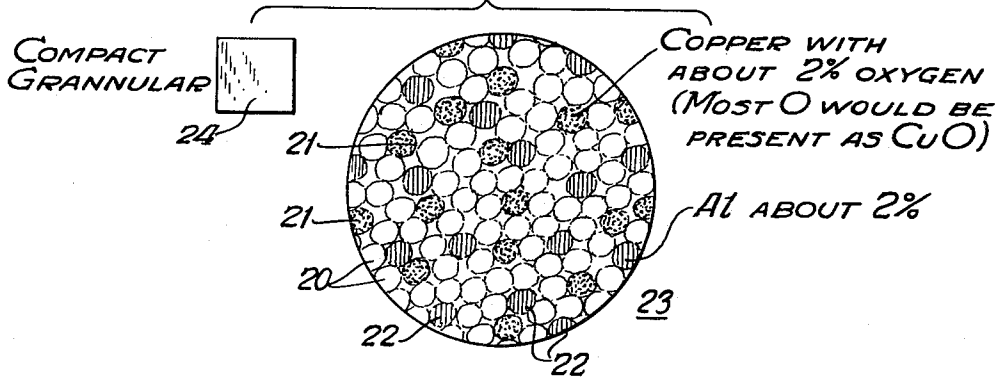


Fig. 6.

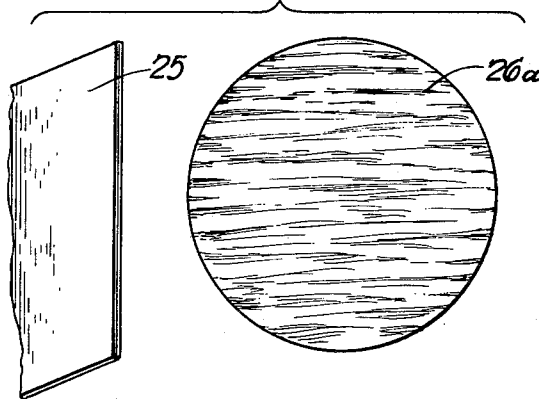
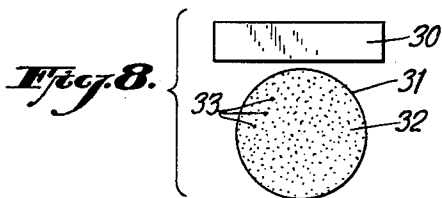
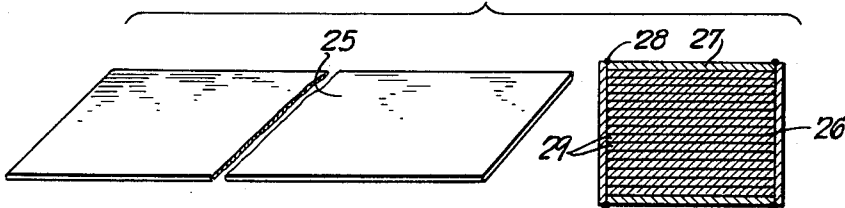


Fig. 7.



INVENTOR.

MILTON B. VORDAHL

BY

John R. Legan
ATTORNEY

1

2

3,205,099 STABLE DISPERSOID COMPOSITES AND PRODUCTION THEREOF

Milton B. Vordahl, Beaver, Pa., assignor to Crucible Steel Company of America, Pittsburgh, Pa., a corporation of New Jersey

Filed June 14, 1961, Ser. No. 117,124

14 Claims. (Cl. 148—4)

This application is a continuation-in-part of application Serial No. 37,953, filed June 22, 1960, now abandoned.

This invention pertains to composite materials and the production thereof wherein a stable dispersoid comprising small particles of metal compounds is uniformly distributed throughout a base or matrix metal.

Heretofore, much effort has been directed to the production of composite materials in this general category with the principal objective of improving the elevated temperature creep strength thereof as compared to that of a base metal. However, the techniques employed and the products resulting therefrom have fallen short not only of achieving this objective but also of achieving other objectives as well.

One process that has been employed involves admixing, in powder form, the basis or matrix metal with metallic carbides, oxides or nitrides, pressing and sintering the resultant mixture and thereafter plastically deforming the same, as by forging or rolling, the latter step being done with the objective of breaking up the metal compounds into small particles and uniformly dispersing the same throughout the basis or matrix metal. However, by actual practice of the foregoing process I have determined that it is incapable of achieving its intended objective. Where, as in the usual case, the metallic compounds are harder and stronger than the basis or matrix metal at the forging or rolling temperature, I have found that the metal compounds are not appreciably broken up and dispersed, being cushioned as they are by the basis or matrix metal which plastically deforms about the compound particles. Further, where the relative hardness and strength of the basis metal during plastic deformation is such that the compound particles are pulverized, I have found that only localized dispersion thereof occurs in the regions of the original sites of said particles. Attempts to achieve the foregoing objective by subjecting the powdered ingredients prior to mixing or prior to mixing and pressing to extended comminution, as by ball milling, are of course limited by economic considerations, and in most cases, such attempts have proven technically or practically impossible of successful operation.

Another process that is exemplary of the prior art utilizes the principle of solid state internal oxidation, wherein a reactant may be oxygen, nitrogen, etc. In that process, an alloy of an active metal and a relatively inactive metal is prepared, as by melting the pure metals or by mixing the same in powder form, compacting, sintering, etc. The alloy is then heated in a suitable atmosphere which supplies a reactive gas such as oxygen to the surface at a suitable rate. The oxygen diffuses into the alloy and reacts internally with the active metal component thereof, forming an oxide dispersoid. Unfortunately, very few systems have been found for which this process yields a desirable product. Usually the oxygen penetrates preferentially along grain boundaries or to other preferred sites. A significant proportion of the active metal also diffuses to such sites and reacts there with the oxygen, the result being a reaction compound in a nonuniform or otherwise undesirable state of dispersion. Even if the alloy be finely comminuted prior to internal oxidation

of the particles, effects such as unavoidable formation of a diffusion-blocking layer on the surface of the particles very often frustrate such effort.

I have therefore, and in accordance with the present invention, attacked the foregoing problem from a basically different concept and successfully solved the same by employing a fundamentally different process from those above described, and also different from other previously known processes heretofore employed.

In accordance with the basic concept of my invention, I form the dispersoid particles, in sub-micron particle size uniformly dispersed throughout the basis metal, by internal reactant exchange during extensive working of a material comprising a relatively inactive basis metal initially containing a reactant in solution or as a dispersion of a dissociable compound and a material composed wholly or partly of a relatively active metal which forms compounds with the reactant. By "dissociable compound" I have reference to relatively unstable or dissociable compounds of the relatively inactive metals herein contemplated with the contemplated reactants. Working is preferably carried out on interleaved foils or admixed granules of the starting materials. The resultant compounds comprise up to about 15% by volume of the basis metal and are ideal for the manufacture of hot creep resistant articles, such as gas turbine blades and the like. The reactant is selected from the group consisting of non-metals of groups 3A, 4A, 5A and 6A of the periodic chart of the elements, i.e., B, C, N, O, Si, P, S, As, Se and Te, and is preferably restricted to an element of the group consisting of boron, carbon, nitrogen, oxygen, silicon and sulfur.

Thus, according to one aspect of the invention, I utilize as the base, a relatively inactive metal such as, for example, rimming steel, containing in solution or as a dispersion of a dissociable compound, a substantial amount of a reactant such as oxygen and/or nitrogen, or, alternatively, I form an alloy of a relatively inactive basis metal and one or more reactants such as the elements oxygen and nitrogen, in amount so calculated to yield about 1 to 15% by volume of refractory compound dispersoid. This I roll into thin strip or foil. I then select a relatively active metal, such as aluminum, which readily forms such compounds with oxygen and/or nitrogen, or I select an alloy of a relatively active metal plus a relatively inactive metal, e.g., an alloy of iron and aluminum. I then roll this metal or alloy into thin strip or foil. I then cut the foils into sheets and stack them in interleaved relation comprising alternating sheets of the basis and the active metals. The stack assembly then may be enclosed in a pack and pack rolled to a large reduction at minimum temperature and with intermediate recovery anneals as required. The pack is then stripped, cut into shorter lengths, assembled in a shorter pack and rolled again, until the sheets or lamellae are of sub-micron thickness.

During the working, fresh, clean surface areas of the base and the active metal lamellae are continuously exposed in surface contact to one another so that the reactant e.g., oxygen and/or nitrogen, diffuses from the inactive metal of the base foils to the interface between the base and active metal lamellae, forming there a layer of sub-micron particles of the active metal compound, e.g., oxide and/or nitride, the size of such particles being controllable by the temperature and rate of working, with high temperatures and low rates of working tending to favor formation of coarser particles, and with prolonged, high temperature anneals also favoring formation of coarse particles, etc. Obviously, any desired degree of refractory compound, e.g., oxide and/or nitride, fineness can be obtained by working at low enough temperatures, since

the reactant is available internally as that carried in solution or as a dispersion of a dissociable compound by the inactive metal, and is available to the active metal only at newly formed interfaces. At high temperatures, the bulk of the reactant may rapidly diffuse to the interfaces and react there with the active metal. In this case, of course, the fineness and distribution of the particles comprising the dispersoid are controlled by the fineness attained by the metals prior to heating. Again, obviously, once exchange has occurred, all reactant is then present as stable, active metal compound, and further working can effect but little additional refinement, although some further favorable distribution of particles may be effected by such work. Attempts to add additional reactant, as oxygen and/or nitrogen, by diffusion from the surface will result merely in thickening of the active metal compound layers at the interfaces—a result which may not be desirable in many cases. Also, complete exchange of internal reactant by a final anneal even after attaining the desired character of dispersion may not necessarily be desirable or necessary, although it would serve to stabilize the structure. Any unreacted portion of the active metal may in some cases during a final anneal alloy with the relatively inactive metal of the base by interdiffusion.

A preferred modification of the above aspect of the invention consists in initially admixing in granular or powder form, the relatively active metal and the base, the latter comprising a relatively inactive metal containing a reactant in solution therewith as aforesaid. Alternatively, if the solubility of the reactant in the relatively inactive metal be undesirably low, a multi-phase alloy of the relatively inactive metal and reactant may be comminuted or rolled to foil, depending on ductility, and substituted for the powder or foil of the base employed in the foregoing. As a further alternative, the relatively inactive metal in substantially pure state may be employed in admixture with a compound composed of the relatively inactive metal and the reactant, said reactant being present in appropriate amount to react with the active metal constituent. The admixture is then pressed into a billet and rolled into a strip. The strip is then cut into sheets, stacked, enclosed into a pack and rolled to a large reduction, the procedure being thence in accordance with that heretofore described. This modified procedure has the practical advantage that it eliminates the initial and separate strip rolling of the inactive and active metals followed by interleaving before pack rolling. In addition, it provides a more intimate and extensive surface contact between the active and inactive metal components throughout the rolling operation, thus facilitating compound formation and uniform dispersion in sub-micron particle sizes. The procedure has the disadvantage that it allows occasional direct contact of particles of the compound composed of the relatively inactive metal and the reactant with particles of the relatively active metal. This results in immediate formation of stable compound composed of relatively active metal and reactant at the site of such contact, and in turn, in occasional undesirably large clusters of such stable compound throughout the final composite. This result is of course more pronounced when free particles of inactive metal compound are present than when such compound exists only as a second phase in the alloy of inactive metal and reactant. In the absence of direct contact between particles of inactive metal compound and particles of active metal, the inactive metal compound dissociates, and the reactant in solution in the inactive metal is depleted by diffusion to the interfaces between the inactive metal and active metal, and reacts there with the active metal to form stable compound of the active metal. Thus, reactant is supplied internally much as though the same were all present in solution in the base.

A still further modification of the invention consists in initially coating or wetting the relatively inactive

metal with the relatively active metal, by admixing in powder or granular form the base and an active metal alloy, the latter consisting of an active metal and a metal which either alloys with the inactive metal or which volatilizes at low temperature. In the latter case the admixture is heated to drive off the volatile metal before extensively working, e.g., compacting and rolling, while in the former case the admixture is simply subjected to extensive working, e.g., compacting and rolling, whereby an internal shearing action is produced effective for the obtention of an intimate internal reactant exchange.

Although the foregoing examples are restricted to obtaining finely divided refractory compound dispersoid by extensive working of very thin foils of metals or alloys containing, between them, the components of the refractory compound, it is to be understood that the same result is obtainable by effecting the essential mechanical working of the metals and/or alloys in other ways.

Having thus described the invention in general terms, reference will now be had for a more detailed description, to the accompanying drawings wherein:

FIG. 1 is a graphical showing of creep strength versus temperature for a stable dispersoid type of composite according to the invention as compared to that of a typical high strength alloy containing no dispersoid.

FIGS. 2 to 4, inclusive, illustrate the aforesaid prior art procedures for preparing stable dispersoid types of composites, and also the metallic structures obtained at successive stages.

FIGS. 5 to 8, inclusive, illustrate the successive steps of preparing stable dispersoid types of composites according to the above mentioned preferred method of the present invention, and also the metallic structures obtained at successive stages.

Referring to FIG. 1, graph A typifies the creep strength-temperature relationship of a stable dispersoid composite, while graph B typifies that of a high strength alloy of the same base, but free of the dispersoid phase. It will be seen that whereas at relatively low temperatures, the high strength alloy has higher creep strength than the stable dispersoid composite, this situation is reversed at temperatures extending upwards of about 350° F. wherein the dispersoid composite maintains substantially its room temperature creep strength while that of the high strength alloy falls off rapidly substantially to zero.

Referring to now FIGS. 2-4, inclusive, illustrating the above mentioned prior art technique for preparing stable dispersoid composites, the first step shown in FIG. 2 consists in admixing in powdered or granular form, particles, as at 10, of the basis or matrix metal, and particles, as at 11, of the metal compound, and compacting into a billet as at 12, as by pressing or pressing and sintering. If now the billet of FIG. 2 is extruded or rolled (as in a sheath) to a small rod, thin strip or foil as at 13 or 14 of FIGS. 3 and 4, respectively, the metal compound particles 11 of FIG. 2, will be broken up and distributed as shown at 15 and 16 of FIGS. 3 and 4, respectively, depending on whether the compounds are appreciably softer or harder than the matrix metal. Referring to FIG. 3, if the metal compounds are easily broken up during the extruding or rolling, they will become finely comminuted as illustrated at 15, but nevertheless will not be uniformly dispersed throughout the volume of the basis metal, but will be distributed about the sites of the original compound particles 11. On the other hand, referring to FIG. 4, if the compound particles are substantially stronger and harder than the matrix metal, the comminution thereof during extruding or rolling will be relatively slight, and the particles comprising the dispersoid will be relatively coarse as at 16 and again distributed locally about the sites of the original particles 11 of FIG. 2. In neither case does the subdivision of the metal compounds extend to sub-micron particle size uniformly dispersed throughout the matrix or basis metal, as is required in order to impart the extremely high, ele-

5

vated temperature creep strength, such as that illustrated by graph A of FIG. 1.

Referring now to FIGS. 5-8, inclusive, illustrating the preparation of a stable dispersoid composite according to a preferred embodiment of the present invention, the first step of FIG. 5 consists in admixing in granular form, a relatively inactive metal, a desired proportion of which is relatively pure, as indicated by the unshaded granules 20 and a desired proportion of which has dissolved therein a substantial amount of reactant, as indicated by the stippled granules 21, or alternatively these granules may be of a compound of the basis metal, i.e., relatively inactive metal, and said reactant, the third constituent of the admixture being granules of a relatively active metal, as indicated by the shaded granules 22. Of the total mix, the active metal is added in an amount calculated to yield about 1 to 15% by volume of refractory compound, and the inactive metal particles containing dissolved reactant or comprising a compound with said reactant are added in an amount sufficient to provide the necessary reactant to react with the active metal present to form the active metal compound during the subsequent working. The resultant admixture shown generally at 23 of FIG. 5 is compacted into a billet as at 24, extruded, and sheath rolled, or otherwise deformed at a temperature just high enough to cause the reactant to interchange at interfaces newly formed during the working, and low enough to prevent formation or growth of particles to more than sub-micron size. In general the higher the work rate, the higher the permissible temperature, although a very wide range of rate and temperature combinations are suitable, depending on original state, on product fineness desired, and on workability of the composite, which usually does not improve with continued reduction. Such work is continued to obtain thin strip or foil as at 25, FIG. 6, to produce a relatively uniform composite structure as illustrated generally at 26a, at which stage the granules 20-22, inclusive, FIG. 5, have been considerably broken up and uniformly dispersed into much smaller, flaky particles, and flattened by rolling and wherein a considerable portion of the reactant has reacted with the active metal to form a compound therewith by internal reactant exchange during the rolling.

To complete the compound formation, comminution and dispersion, the foil strip 25 is now cut into sheets, which are stacked as at 26, FIG. 7, and enclosed in a metal casing or pack, as at 27, welded along the seams as at 28 to exclude air, and rolled to a large reduction, such that the individual lamellae, such as 29 of the pack 26 are rolled to sub-micron thickness. If necessary to accomplish this, after the initial pack rolling, the pack 27 may be stripped and the rolled pack 26 cut again into sheets, stacked, repacked and re-rolled.

As the rolling proceeds, fresh surfaces of the active metal constituent are continually exposed and re-exposed to the reactant supplied by the base, whereby the active metal is converted by internal reactant exchange into particles of a compound with said reactant which are of sub-micron particle size uniformly dispersed throughout the basis metal, while meantime the basis metal has consolidated into an integral structure with which any excess or unreacted active metal may be alloyed by interdiffusion. If necessary, in order to complete the reaction, the resultant composite may be given a final high temperature anneal to complete the reactant exchange and to stabilize the structure.

Referring to FIG. 8, the resultant composite is shown at 30 and its structure, on a greatly magnified scale, at 31, and consisting of the matrix or basis metal 32 having uniformly dispersed throughout the same the active metal-reactant particles, as at 33, reduced to sub-micron particle dimensions. All of the basis metal-reactant compound has now dissociated, and the reactant in solution diffused to interfaces of the finely dispersed metals as described.

6

Exemplary of stable dispersoid composites produced in accordance with the above-described procedure is a material comprising copper as the "inactive" basis metal with particles of aluminum oxide, sub-micron in size, forming the stable dispersoid. A starting mix therefore could comprise granules of copper having about 2% oxygen dissolved therein and granules of metallic aluminum, the latter granules comprising about 2% by weight of the total mix.

Similarly, the inventive method contemplates the production of a material comprising titanium as the "inactive" basis metal with particles of gadolinium oxide, sub-micron in size, forming the stable dispersoid. A starting mix therefore is, e.g., granular titanium having about 2% oxygen dissolved therein and granular metallic gadolinium or gadolinium alloy, the gadolinium comprising about 15% by weight of the total mix.

Comparing now the preparation of stable dispersoid composites according to the procedure of the present invention as illustrated in FIGS. 5-8, inclusive, with that or prior art techniques above discussed and as illustrated in FIGS. 2-4, inclusive such prior attempts to "micronize" the metal and compound constituents 10 and 11, respectively, of FIG. 2, have been frustrated by breakup and spheroidization of the metal filaments or lamellae formed during working and as they approached micron dimensions. With the procedure of the present invention, as illustrated in FIGS. 5-8, inclusive, however, the metal interfaces newly formed during working constitute sites of continuous formation of active metal-reactant compound by internal reactant exchange, and spheroidization is completely blocked.

Reverting to the prior art techniques, obviously no amount or method of working of mixed powders containing a previously formed refractory metal oxide or nitride can accomplish the same result, since little if any effective refinement of the refractory oxide or nitride will result from working. That is, the particle size of the refractory metal oxide or nitride as initially introduced into admixture with the matrix metal, is essentially fixed by that obtained when the mixture is made, with results as illustrated in FIGS. 3 and 4 following rolling.

Reverting again to the procedure of the present invention, as illustrated in FIGS. 5-8, inclusive, in order to assure the presence of adequate reactant in the relatively inactive metal, it may be necessary, as above stated, to incorporate low stability compounds of the metal itself therein, as would be required where a basis metal is employed in which the reactant will not dissolve or form a solid solution therewith in sufficient amount. During working and reactant depletion of the base, such incorporated compound will simply dissociate, with the metal thereof diffusing into the basis metal and the reactant diffusing to the interfaces formed, there to react with the relatively active metal. Working and intermediate annealing temperatures must be low enough to prevent macro diffusive movement of the reactant. Short range interstitial movement is of course greatly accelerated during working.

The handling of very fine powders of very active metals, such as calcium, magnesium, thorium, etc., is difficult owing to premature formation therein of much stable oxide or even combustion of the metal powder due to air exposure while admixing with the relative inactive basis metal, where such highly active metals are employed for producing composites according to the present invention. In order to prevent premature oxide formation, which is destructive of the purposes of the invention, such highly active metals, where employed, may be pre-alloyed with another metal which either volatilizes at relatively low temperature or which will alloy by interdiffusion with the basis metal. Thus, in accordance with this modification of the invention, the basis metal in powdered form may be admixed with the active metal alloy likewise in powdered form, thus to coat or wet the basis metal

particles with the active metal pre-alloy. If the pre-alloy is formed of an active metal and a volatile metal, the admixture may be heated to volatilize or drive off the volatile constituent before compacting and rolling. On the other hand, if the pre-alloy is formed of an active metal and a metal which alloys with the basis metal, the admixture is simply compacted and rolled in accordance with the procedure above described.

The following is an illustrative example of the inventive procedure: Titanium powder is heated in a suitable oxygen containing stream at an appropriate temperature to form a titanium-oxygen alloy containing about 1% by weight of oxygen. The resultant alloy is annealed in vacuum (an inert gas, e.g., argon, may be used) at about 1400° F. whereby the oxygen contained therein diffuses inwardly to leave clean surfaced metal particles. So treated, titanium-oxygen alloy particles are coated or wet with powdered tin-calcium alloy by admixture therewith and then compacted and rolled as aforesaid. As the rolling proceeds the tin component of the active metal alloy diffuses into and alloys with the titanium, while the active metal, i.e., calcium, is left on the surfaces of the inactive metal alloy particles to react with the oxygen therein by internal oxygen exchange.

As a further illustrative example of the foregoing procedure, a relatively inactive metal such as columbium in powdered form may be oxygenated at about 1100° C. to the extent of about 4 atomic percent oxygen. The so-oxygenated columbium powder is then wetted or coated by admixing with powdered zinc-zirconium alloy (alternatively, powdered thorium-mercury or calcium-mercury alloy may be employed). The admixture is heated prior to compacting, to drive off the volatile zinc (or mercury), said heating in all cases being conducted in vacuum or inert atmosphere.

As illustrative of various other composites that may be produced in accordance with the invention, titanium in powdered form may be oxygenated to the extent of about 2% by weight and admixed with a magnesium-tin (or a magnesium-mercury) pre-alloy such as to add to the admixture about 2% by weight of magnesium, and the admixture processed in the manner above set forth. Alternatively, titanium powder oxygenated to the extent aforesaid may be admixed with a pre-alloy in powdered form containing calcium (or thorium) in amount slightly beyond that required to react with the oxygen contained in the base. Similarly, columbium may be employed as the basis metal and magnesium, zirconium or thorium as the active metal, or tungsten may be employed as the basis metal and thorium as the active metal.

An additional advantageous aspect of the preparation of composites according to the present invention is the effective removal of reactants normally present as impurities in the basis metal, e.g., O, N, C and S, by reaction thereof with the active metal to form stable compounds therewith of sub-micron particle size which are uniformly dispersed throughout the basis metal whereby the inherent strength, toughness and ductility of the pure basis metal is not adversely affected. As regards this aspect of the invention, it should be pointed out that where efforts are made to remove residual reactants from metals by liquid state reaction with a more active metal, this usually results in inter-dendritic segregation of the stable compounds formed unless they are allowed to float out of the bath. This segregation in turn often results in limited ductility gain, if any, with little or no strength benefit, especially if an appreciable volume percent of the compounds remain, because the compound distribution cannot be controlled. Likewise internal oxidation of active metal alloys often results in undesirable compound distributions. On the other hand, solid state internal reactant fixation in accordance with the procedure of the present invention, permits better control and thus, better and more consistent uniformity of distribution in the final product.

Obviously this second aspect of the invention has as its object a product which differs substantially from that of the first aspect, although the process used may be construed as being identical. In the first aspect, the object is to strengthen a basis metal against high temperature creep by forming therein a large amount, for example, about 1 to 10%, or preferably about 2 to 4%, depending on fineness, of a stable dispersoid, comprising particles, sub-micron in size, and uniformly dispersed throughout the basis metal, said particles consisting of an active metal-reactant compound. In the second aspect, the object is to improve ductility of a metal or alloy by fixation of the small amount—usually a very small fraction of 1%—of interstitials (oxygen, nitrogen, carbon, etc.) normally present in “pure” metals, and to do so in a manner which distributes the fixed interstitial content in a manner least damaging to ductility, namely, as a uniform dispersion.

As an example of the second aspect, hydrogen-reduced, tungsten powder is mixed with a small amount, for example, up to ½%, of pure thorium or hafnium powder, compacted and extruded or sheath rolled, all in vacuum or inert atmosphere, and at minimum temperature consistent with workability. The resulting solid tungsten admixed with dispersed thorium oxide or hafnium oxide in trace amount, plus trace amount of unreacted thorium or hafnium, is exceptionally ductile, with a ductile to brittle transition temperature lower than otherwise obtainable. Again, both aspects of the invention depend for success on the process of solid state, internal reactant exchange, but have obviously quite different end products as objects.

The following table, merely illustrative and by no means all-inclusive, gives a number of examples amenable to the inventive procedure and covered by the principle of solid state internal reactant exchange:

Inactive metal	Reactant	Active metal
Cu, Ni, Co, Fe, Ch. Mo, W. (alone or in combination).	O-----	Al, Mg, Th, Hf, Ti, Zr, Gd, Ba, Ca.
Ti, Zr, Fe, Ni, Cu-----	O-----	Th, Gd, Ca, Mg.
	N-----	Al, Mg, Ca, Sc, La, Ce, Ti, Zr, Hf, Th, Ta, U.
Fe, Ni, Co-----	C-----	Hf, Ta, Ti, U, Ch, V, Zr.
Mo, W-----	C-----	Ti, Ta, Hf.
Cu, Ni, Co-----	B-----	Ti, Zr, Hf.
Cu, Ni, Fe, Co, Cr-----	S-----	Sr, Ba, Ca, Mg, Ce, La.
Cu, Ni, Co, Cr, Fe, Mo, Co.	Si-----	Ti, Zr, Hf.

Throughout the foregoing, the terms “inactive” and “active” are intended as relative with respect to the reactant involved. It is to be understood that any one of the “active” metals, appearing in the foregoing tabulation, may be used, either as the pure metals themselves, or as alloys thereof with others of the contemplated active metals or with one or more of the contemplated “inactive” metals, so long as the basic principle of the invention is observed, i.e., in no event is any one of the metals or alloys to contain all components of the refractory compound. As aforesaid, it is not intended that metals and/or alloys of extremely high purity are required, but the full advantage of the invention is not realized unless most of the refractory compound is produced as a result of internal reactant exchange during extensive working. To the extent that both reactant and “active” metal are present in a single metal or alloy, uncontrolled prior presence or formation of stable refractory compound will result. This is tolerable, of course, only to a small degree within the intent of the invention.

It is to be noted that while numerous examples representative of the practice of the invention have been disclosed many others could be cited which would come within the purview of the invention by virtue of there being no substantial departure in spirit or scope there-

from, the basic requirements in all such cases being that the active metal-reactant compound be stable, i.e., maintain its identity and particle size in contact with the inactive metal at all process and use temperatures, and comprise particles sub-micron in size and uniformly dispersed throughout the inactive metal.

What is claimed is:

1. The method of producing a stable dispersoid composite material which comprises: intimately contacting, in the solid state, a base material and a relatively active metal material, said base material containing a relatively inactive metal material and at least one reactant selected from the group consisting of B, C, N, O, Si, and S, and extensively mechanically working, while so contacting, said base and relatively active metal materials to continually expose to each other their fresh surfaces whereby reaction therebetween is promoted to form particles of stable compounds of relatively active metal and reactant uniformly dispersed throughout said composite material.

2. The method of producing a stable dispersoid composite material which comprises: intimately contacting, in the solid state, a base material and a relatively active metal material, said base material comprising at least one member selected from the group consisting of a relatively inactive metal containing in solution a substantial amount of a reactant, a compound of a relatively inactive metal and a reactant, a mixture of a relatively inactive metal and a compound of a relatively inactive metal and a reactant, and mixtures thereof, wherein said reactant is at least one member selected from the group consisting of B, C, N, O, Si and S, and said relatively active metal material comprising at least one member selected from the group consisting of a relatively active metal, an alloy of a relatively active metal, and mixtures thereof, and extensively mechanically working, while so contacting, said base and relatively active metal materials to continually expose to each other their fresh surfaces whereby reaction therebetween is promoted to form particles of stable compounds of relatively active metal and reactant uniformly dispersed throughout said composite material.

3. The method of claim 1 wherein the step of intimately contacting is carried out by admixing, in comminuted form, said base material and said relatively active metal material, and compacting the resultant admixture.

4. The method of claim 1 wherein the step of inti-

mately contacting is carried out by rolling said base material into thin strip, rolling said relatively active metal material into thin strip, cutting said strips into sheets, and stacking said sheets in interleaved relation comprising alternating sheets of base material and relatively active metal material, and the step of extensively mechanically working is carried out by pack rolling the stacked sheets.

5. The method of claim 3 including the steps of rolling the compacted admixture into thin strip, cutting said strip into sheets, and stacking said sheets in interleaved relation, and the step of extensively mechanically working is carried out by pack rolling the stacked sheets.

6. The method of claim 4 wherein said pack rolling is continued until said alternating sheets of base material and relatively active metal material are sub-micron in thickness.

7. The method of claim 5 wherein said pack rolling is continued until the individual sheets comprising said stacked sheets are sub-micron in thickness.

8. The method of claim 1 wherein said reactant comprises boron.

9. The method of claim 1 wherein said reactant comprises carbon.

10. The method of claim 1 wherein said reactant comprises nitrogen.

11. The method of claim 1 wherein said reactant comprises oxygen.

12. The method of claim 1 wherein said reactant comprises sulphur.

13. The method of claim 1 wherein said reactant comprises silicon.

14. The method of claim 1 wherein the step of extensively mechanically working is accompanied by the step of heating said base and relatively active metal materials.

References Cited by the Examiner

UNITED STATES PATENTS

1,675,867	7/28	Pike	75-47
2,028,240	1/36	Palmer	75-226
2,100,537	11/37	Conway	75-47 X

DAVID L. RECK, *Primary Examiner*.

RAY K. WINDHAM, *Examiner*.