

[54] **CONSOLIDATED COMPOSITE MATERIALS BY POWDER METALLURGY**

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**Related U.S. Application Data**

[63] Continuation of Ser. No. 849,133, Aug. 11, 1969, abandoned, which is a continuation-in-part of Ser. No. 709,700, March 1, 1968, Pat. No. 3,591,362.

[52] U.S. Cl. .... **75/0.5 BC**

[51] Int. Cl. .... **B22f 9/00**

[58] Field of Search .... **75/0.5 BC**

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[57] **ABSTRACT**

Directed to the powder metallurgy production of consolidated metal products wherein the starting material comprises dense wrought particles containing at least 15 percent by volume of a compressively deformable metal with the remainder being one or more other metals or non-metals with the internal structure of the particles being non-porous and with the constituents thereof being intimately united and interdispersed, i.e., mechanically alloyed, said particles, upon consolidation, yielding metal or cermet products having unusual properties and capable of compositional characteristics not available as a result of other processing techniques.

**3 Claims, 4 Drawing Figures**

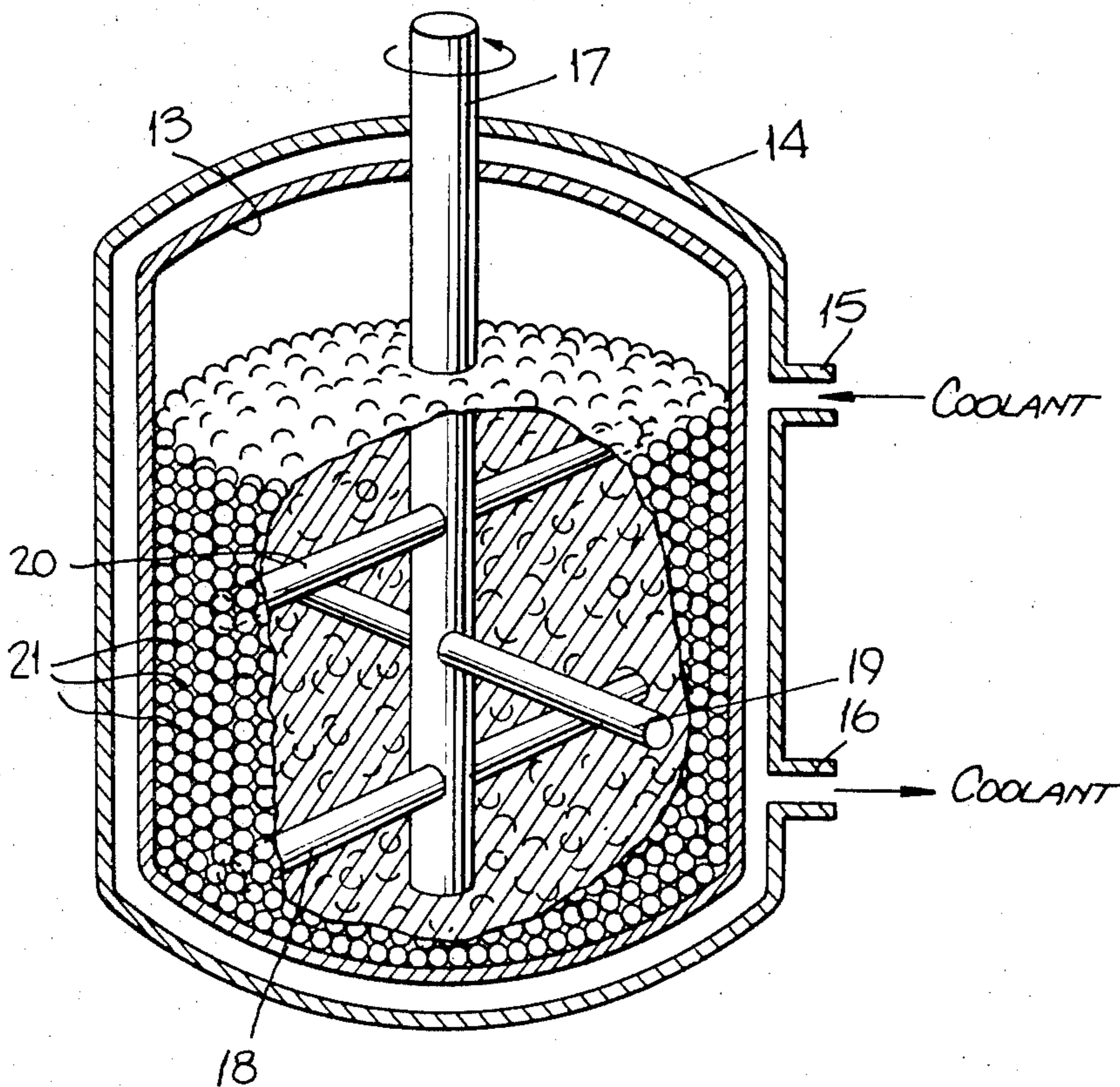


Fig. 1.

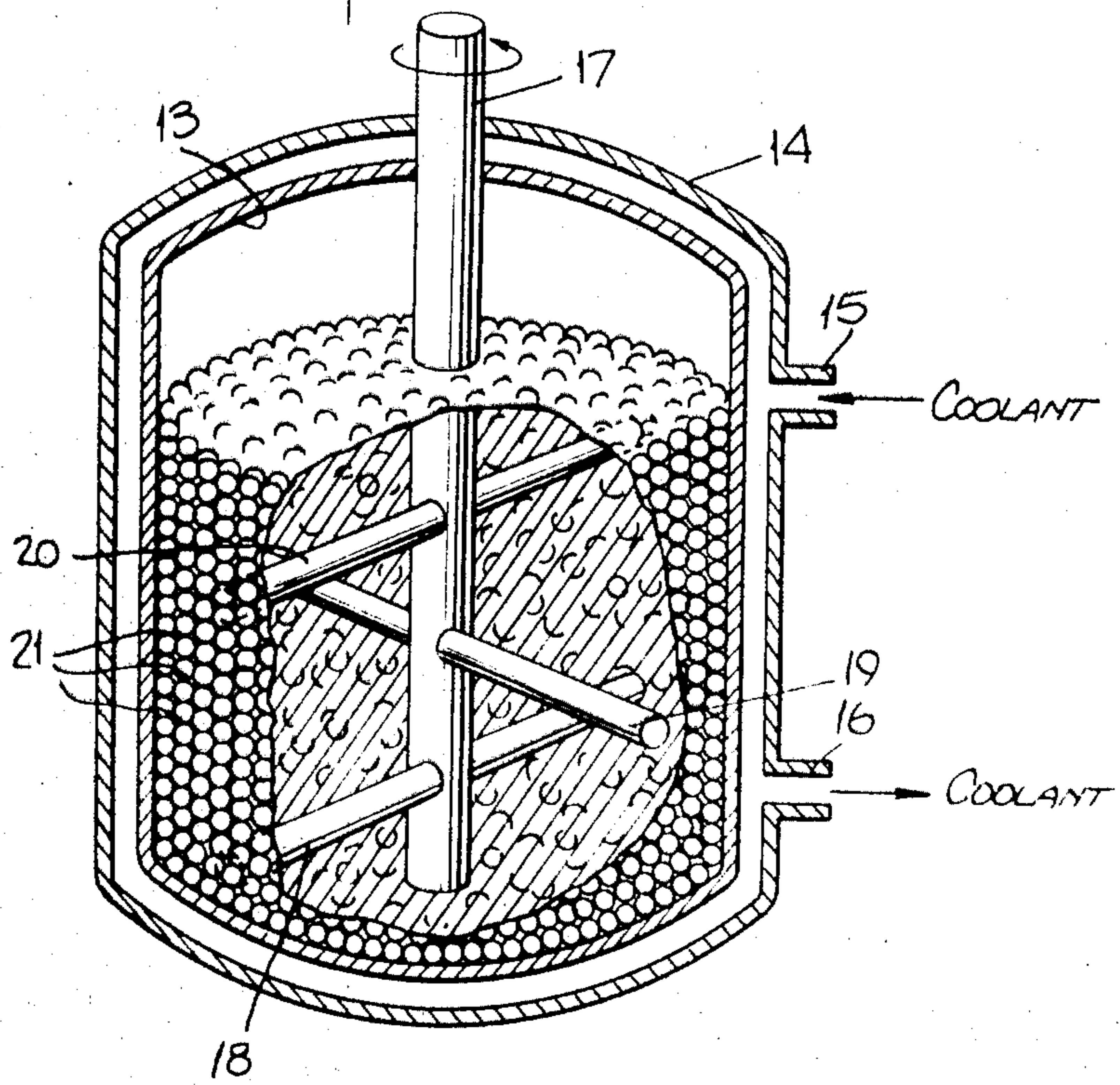
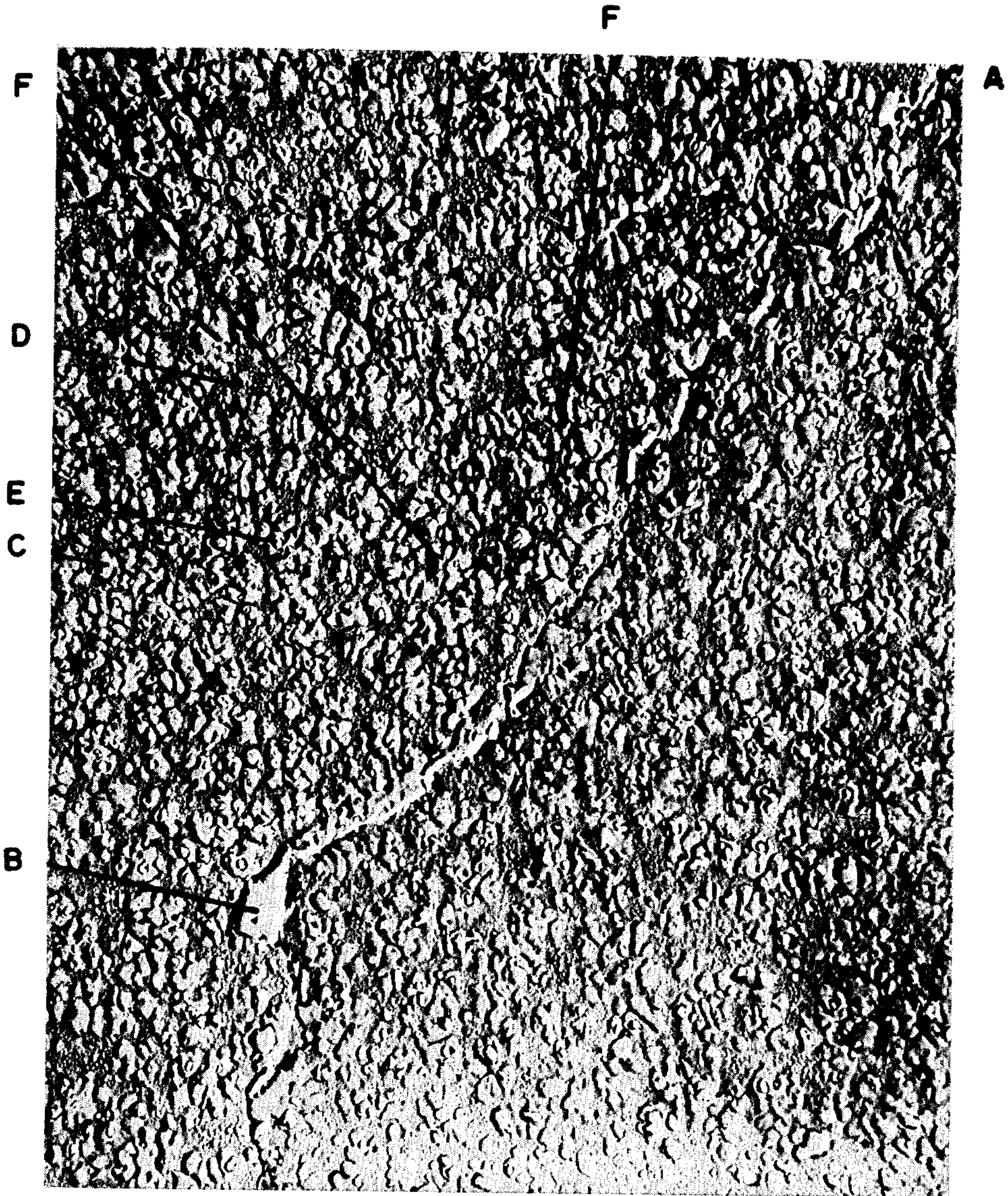


Fig. 2.





A'

Fig. 3.

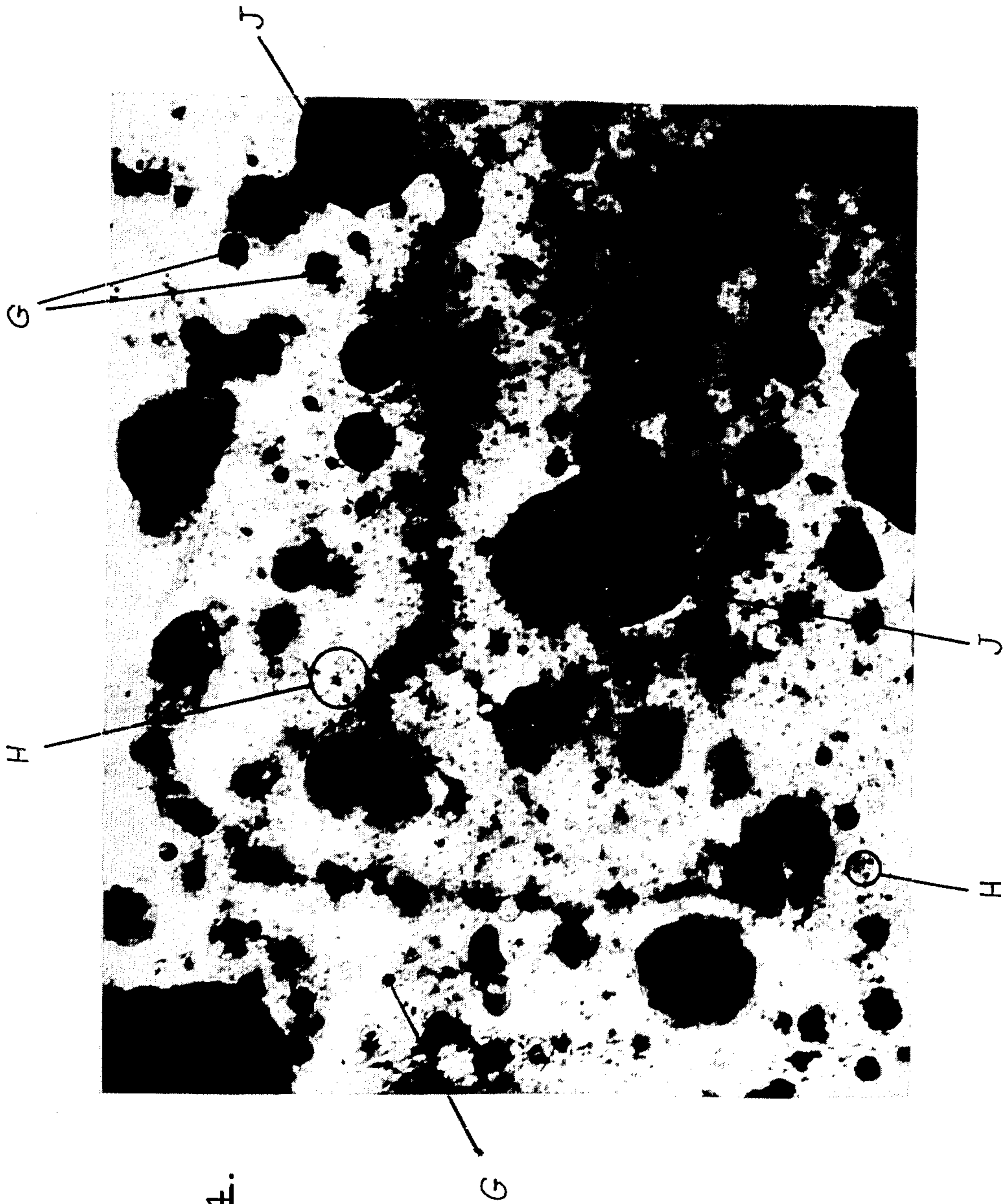


Fig. 4.

## CONSOLIDATED COMPOSITE MATERIALS BY POWDER METALLURGY

The present application is a continuation of Ser. No. 849,133, filed Aug. 11, 1969, now abandoned, which is in turn a continuation-in-part of U.S. application Ser. No. 709,700 filed Mar. 1, 1968 now U.S. Pat. No. 3,591,362.

This invention relates to metal products and to their production by powder metallurgy.

When metal products are made by melting, numerous problems arise. These include the occurrence of dendrites and other forms of segregation in castings of complex alloys, which lead to difficulties in working and with non-uniform response to heat treatment. Brittle segregates impair the ductility of the cast material. If the segregates are of a very low melting composition they may lead to the phenomenon known as "hot shortness" severely limiting the permissible hot working range, and even when working is possible segregated regions persist in elongated form which give rise to anisotropic properties and other disadvantages.

These problems may to some extent be overcome by the techniques of powder metallurgy, which is also the most convenient way of producing dispersion-strengthened metals and alloys and other products consisting of finely divided immiscible constituents. Nevertheless, powder metallurgy presents other problems of its own.

Since the possibility of homogenization is limited to that which can be brought about by sintering, thermal diffusion in the solid state and localized melting, a starting material is required that contains the constituents in a finely divided and uniformly distributed condition. Thus, in making an alloy from a mixture of elemental powders the powders must be very fine, e.g., 25 or 10 or even 3 microns or less in size, so that the alloy can be rendered homogeneous by diffusion in a reasonably short time, and such powders tend to be pyrophoric and to pick up impurities, such as oxygen from the atmosphere, which contaminate and adversely affect products made from them. Mechanically mixed powders of different densities also tend to segregate on storage and handling of the mixture, leading to non-uniformity in products made from the mixture.

To avoid the need for mechanical mixing, pre-alloyed powders may be used, for example, those made by atomisation from a molten bath of the alloy, but these are expensive, difficult to obtain with controlled particle size, and may even contain substantial dendritic segregation.

Similar difficulties arise in making dispersion-strengthened metals and alloys by consolidating mechanical mixtures of the constituents. Here, especially fine metal powders are desirable, with the associated risk of contamination, and there are also the further problems that the refractory dispersoid particles tend to flocculate owing to static electrical charges and that constituents of different densities tend to segregate on storage and handling of the mixture. Flocculation and segregation both lead to non-uniformity of the final wrought product owing to the formation of stringers of dispersoid particles and adjacent areas impoverished in the dispersoid.

Such stringers and associated defects are deleterious to structural elements used under stress, particularly at high temperatures. The impoverished regions do not

contribute significantly to the strength of the product, and a body in which the impoverished areas constitute more than 10 percent by volume will be significantly weaker than one without such defects. In addition, the gross concentrations of refractory particles within the stringers themselves provide sites for stress concentration and can be an important factor in causing failure at elevated temperatures, especially by fatigue.

Non-mechanical processes of producing mixtures of metal and non-metal particles for consolidation include the internal oxidation process, in which a powder, e.g., nickel or copper containing a reactive solute element such as aluminium, silicon, titanium, zirconium or thorium, is selectively oxidised to form fine refractory oxide particles dispersed through the metal matrix. This process also requires fine metal particles; is generally limited to simple binary alloy systems; and furthermore is difficult to apply to chromium-containing nickel-base alloys and stainless steels without oxidising the chromium. Thus, this method is generally only applicable to simple systems such as Ni-Al, Cu-Al, Ni-Th or Cu-Si, where the free energy of formation of the oxide of the matrix metal is up to 80,000 calories/gram atom of oxygen. If however the whole of the alloy powder is first oxidised and then selectively reduced to leave the refractory oxide it is difficult to reduce the matrix oxide completely, particularly if it includes oxides of such metals as chromium, aluminium and titanium.

Various wet techniques have also been proposed for the production of dispersion-hardened metals and alloys. The ignition surface coating process involves coating metal or alloy powders with a decomposable salt of the intended refractory oxide dispersoid by mixing the particles with a solution of the salt and evaporating the liquid. Thus, nickel powder may be mixed with a solution of thorium nitrate in alcohol. The coated powder is then heated in an inert or reducing atmosphere to convert the salt to the corresponding oxide, as particles which coat the surface of the metal particles. Here again, the need for fine metal powders in order to achieve close spacing of the dispersoid particles introduces the risk of contamination; care must be taken to avoid pyrophoric combustion of the powder when it is treated to decompose the salt; and segregation may occur since the last of the liquid to evaporate tends to be very rich in the salt. Microstructures of wrought metal products produced by this method tend to show stringers of dispersed oxide.

In the selective oxide reduction process an intimate mixture of metal oxides, one of which is reducible while the other provides the dispersed oxide phase, is made, for example, by co-precipitating the hydrates of the metals, converting them to oxides, and selectively reducing the matrix metal oxide to metal. The resulting powders can be extremely fine and pyrophoric and, therefore, highly susceptible to contamination. This and other wet methods present difficult materials handling problems, tend to be messy, and are usually costly.

It has been proposed in U.K. Specification No. 821,336 to employ, as starting materials for powder metallurgical processes, powders comprising composite particles consisting of a high-melting point, hard refractory material and a ductile metal, the particles of one constituent being coated by the other. The methods of making such particles described include the chemical or vapour phase deposition of metal on the

refractory particles, and the production on particles of the ductile metal of a surface layer of a metal forming a refractory oxide which is then oxidised. Similar particles result from the conventional ball-milling of mixtures of a ductile metal and a refractory oxide, e.g., mixtures of nickel and thoria, for prolonged periods at the usual ball-to-powder ratios, e.g., up to 3:1. All composite powders of this type have the disadvantage that the particle size of the metal core of the particle is essentially that of the initial powder used and that this relatively coarse structure is carried over into wrought products made from the powder, leading to stringers of dispersoid and associated dispersoid-free areas.

In making powder-metallurgical products from metals normally immiscible in the liquid and/or solid, e.g., iron and copper, a skeleton sintered from powder of one metal may be infiltrated with the other molten metal, or a mixture of the two metal powders may be sintered. Whichever method is used, the distribution of the copper is limited either by the size of the pores in the skeleton or by relative size of the starting powders. The presence of a liquid phase during the infiltration or sintering also tends to cause microsegregation.

The present invention overcomes these various difficulties and provides consolidated metal products having a very high degree of microstructural uniformity and isotropy and substantially free from segregation and stringers.

Objects and advantages of the invention will become apparent from the following description and the accompanying drawing in which:

FIG. 1 is a schematic representation of an attritor of the stirred ball mill type capable of providing agitation milling to produce composite powders for use in accordance with the invention;

FIG. 2 is a reproduction of a photomicrograph taken at 100 diameters showing in longitudinal section a microstructure of a dispersion-strengthened superalloy provided in accordance with the invention after an anneal at 2,250°F. for 4 hours in argon; and

FIG. 3 is a reproduction of an electron photomicrograph taken at 10,000 diameters of a surface replica of a dispersion-strengthened superalloy shown in FIG. 2;

FIG. 4 is an electron transmission photomicrograph taken at 100,000 diameters showing the structure of another dispersion-strengthened superalloy provided in accordance with the invention.

Broadly stated, the invention contemplates the production of consolidated metal products characterised by a high degree of microstructural uniformity and substantially devoid of segregation and stringers by consolidation, e.g., by hot extrusion, hot pressing, forging, etc., unique composite wrought metal particles containing at least 15 percent by volume of a deformable metal with the remainder being a metal or a non-metal, said particles having an interdispersed, mechanically alloyed internal structure.

A non-dispersion strengthened product is to be regarded as substantially free from stringers or segregation if it contains less than 10 volume percent of stringers or of regions exceeding 25 microns in minimum dimension in which there is a significant composition fluctuation from the mean, that is to say, a deviation in composition exceeding 10 percent of the mean content of the segregated alloying element. The boundaries of a segregated region are taken to lie where the composi-

tion deviation from the mean is one-half of the maximum deviation in that region. Regions of composition deviation of less than 25 microns in minimum dimension are not regarded as segregated regions. Preferably, the minimum dimension of the stringer or region of compositional fluctuation does not exceed 10 microns. Preferably, also the proportion of stringers or of segregated regions is less than 5 volume percent. Compositional variations on the scale discussed above may, for example, be detected and measured by electron microprobe examination.

The products are advantageously made, according to the invention, by the consolidation of special composite powders. These powders and methods for their production are described and claimed in U.S. application No. 709,700, now U.S. Pat. No. 3,591,362.

The powders used consist of wrought composite particles having a cohesive, non-porous internal structure made up of two or more intimately united and interdispersed constituents, at least one constituent, amounting to at least 15 percent by volume of the particles, being a compressively deformable metal, and the composite particles individually having substantially the composition of the powder. The internal structure of the composite particles may be regarded as a mechanical alloy.

The constituents of the composite particles, other than the deformable metal, may be other metals or non-metals, including refractory oxides and other hard phases useful for dispersion-strengthening alloys. The term metal in this specification and claims is to be understood as including alloys.

The average spacing between the sub-particles of the constituents interdispersed in the composite particles should be as small as possible in order to facilitate thermal diffusion of inter-diffusible constituents when they are heated to promote alloying. Advantageously, it does not exceed 10 microns and preferably, especially in the case of dispersion-strengthened products, does not exceed 3 microns or even 1 micron, and it may be much less than 1 micron, while the composite particles conveniently average from 20 to 200 microns in size, though larger particles may be used where it is possible to make them with a fine enough internal structure, and smaller particles can be used when the systems involved are sufficiently noble to avoid pyrophorocity.

It will be appreciated that the advantage of using such wrought composite particles to form consolidated powder metallurgy products arises from the fact that the particles act as building blocks for the final structure, the high degree of uniformity of each of the composite particles being carried forward and maintained in the final wrought product. Conversely, the use of inhomogeneous composite particles containing dispersoids for making consolidated products will not lead to homogeneous products. The spacing between the constituents in the product will of course depend on the amount of reduction occurring during the consolidation, and the spacing will generally be less than in the powder particles.

Spacings less than 3 microns or even 1 micron, preferably very much smaller, are particularly advantageous in the case of powders containing refractory dispersoids.

The powder particles are advantageously in a heavily work-hardened condition, as this accelerates alloying of constituents by thermal diffusion on heating, and fa-

cilitates hot deformation as, for instance, hot extrusion for consolidation of a confined mass of powder particles. This is believed to be due to the very fine grain structure resulting from a coalescence of the work-hardened structure upon heating for hot deformation.

The powder may be made, according to our previous application, by subjecting a mixture consisting of at least 15 percent by volume of a compressively deformable metal powder with one or more other metal or non-metal powders to dry, high energy impact milling, suitably in a stirred attritor ball mill, sufficiently energetic and sufficiently prolonged to reduce the particles of deformable metal to less than half, and preferably to less than one-fifth or even one-tenth of their original thickness and to comminute and bond together the constituents of the mixture to form composite, non-porous wrought particles having a cohesive inter-dispersed internal structure. To produce the desired structure the milling may be continued, under conditions in which work-hardening occurs, at least until the hardness of the composite particles has been increased by half the difference between the base hardness and the constant saturation hardness reached on prolonged milling. During energetic dry milling composite particles are repeatedly fractured and reformed by cold working, with a progressive increase in the uniformity of the composition of the particles and the refinement of their internal structure. Advantageously, the powder is milled to saturation hardness, and preferably milling is continued beyond this point until the structure has been refined to the desired extent. Milling beyond the point of saturation hardness is particularly desirable in the case of complex alloys, since these attain saturation hardness while their structure is less uniform than in the case of unalloyed metals, owing to the hardening effect of other hard constituents, e.g., fragments of master alloys.

The composite particles thus comprise comminuted fragments of the initial metal particles welded or metallurgically bonded together, the minimum dimension of the fragments being usually less than one-fifth and preferably less than one-tenth of the average dimension of the initial product from which the fragment was derived. Refractory particles included in the initial powder became distributed throughout the individual composite particles in a fine state of dispersion approximately equal to the minimum dimension of the fragments. Thus, the average distance between the refractory particles in the composite particles is much less than the dimension of the initial metal particles, and is advantageously less than 1 micron, and down to 0.5 micron or less. In such particles there are essentially no islands or areas in the composite particles free from dispersoid.

Dry, high energy impact milling may suitably be performed in a stirred attritor ball mill comprising an axially vertical stationary cylinder containing a charge of balls and having a rotatable agitator shaft located coaxially of the mill with spaced agitator arms extending substantially horizontally from it and serving to maintain the bulk of the ball-charge in continuous relative motion. Such a mill is described in Perry's "Chemical Engineer's Handbook," Fourth Edition, 1963, at page 8-26, and is shown diagrammatically in FIG. 1 of the accompanying drawings, which shows in partial section an upright cylinder 13 surrounded by a cooling jacket 14 having inlet and outlet ports 15 and 16 respectively

for circulating water or other coolant. A shaft 17 is coaxially supported within the cylinder by means not shown and has horizontally extending arms 18, 19 and 20 integral with it. The mill is charged with balls 21 to a depth sufficient to bury at least some of the arms.

The milling time  $t$  required to produce a satisfactory dispersion; the agitator speed  $W$  (in r.p.m.); the radius,  $r$ , of the cylinder (in cm.) and the volume ratio  $R$  of balls to powder are related by the expression:

$$1/t = K W^3 r^2 R$$

where  $K$  is a constant depending upon the system involved. Thus, once a set of satisfactory conditions has been established in one mill of this type, other sets of satisfactory conditions for this and other similar mills may be predicted by use of the foregoing expression.

Except where it is otherwise specified, the dry impact milling referred to in each of the examples in this specification was performed in a water cooled mill of this type. The rate of milling specified in r.p.m., is the rate of rotation of the agitator. Unless otherwise specified the mill was sealed to prevent access of air during milling other than that initially present.

Other mills that can be used include vibratory ball mills, high-speed shaker mills and planetary ball mills. Whatever type of mill is employed, the balls or other attritive elements must be hard and tough enough to compress the deformable metal and are preferably of metal or cermet, e.g., steel, stainless steel, nickel or tungsten carbide; of small diameter relative to the mill; and of essentially uniform size. For further details of the production of the powders, reference should be made to U.S. application No. 709,700.

The composite powders may have an extraordinarily wide range of compositions, and may be used to produce a correspondingly wide variety of composite products. The compositions include a very wide range of metal systems, corresponding to both simple binary and more complex alloys, provided that they include a compressively deformable metal.

The simple alloys include those based on lead, zinc, aluminium and magnesium, copper, nickel, cobalt, iron and the refractory metals. More complex alloys include the well-known heat-resistant alloys, e.g., those based on nickel-chromium, cobalt-chromium, and iron-chromium systems containing one or more alloying additions such as molybdenum, tungsten, niobium, tantalum, aluminium, titanium, silicon, zirconium and the like, with or without non-metals such as carbon and boron.

Dispersion-hardened wrought alloys, both simple and complex, may be produced from composite powders having uniform dispersions of a hard refractory compound phase. The refractory compounds include oxides, carbides, nitrides, borides of such refractory metals as thorium, yttrium, zirconium, hafnium, titanium and even such refractory oxides as those of silicon, aluminium, cerium, uranium, magnesium, calcium, beryllium and the rare earth oxide mixture, didymia. The refractory oxides generally useful as dispersed phases are those whose negative free energy of formation per gram atom of oxygen at about 25°C., is at least about 90,000 calories and whose melting point is at least that of the matrix. The proportion of hard phases may be sufficient to produce cermet compositions so long as sufficient ductile metal is present to provide a host ma-



trix for the hard phase or dispersoid. Where only dispersion strengthening of wrought compositions is desired, as in high temperature alloys, the amount of dispersoid may range from 0.05 percent to 25 percent by volume and, more advantageously, from 0.05 percent to 5 percent or 10 percent by volume.

The process of the invention is also particularly useful in producing wrought products from metal systems whose components have limited or even substantially no mutual solubility in the liquid state and/or solid state, for example, lead or iron with copper, tungsten with copper or silicon, and chromium with copper. It is particularly to be noted that because the constitution of the composite powders is that of an extremely fine-structured mechanical alloy, their compositions and thus that of the products made from them is not limited by normal practical considerations using melting techniques or conventional powder metallurgical techniques and that the substantial absence of segregation in the products leads in many cases to a remarkable improvement in workability as compared with cast alloys of the same composition. Many novel and advantageous alloy compositions thus become available in wrought forms.

The numerous advantages of the use of the wrought composite particles for making consolidated powder-metallurgy metal products include the protection of reactive components such as chromium, aluminium and titanium from oxidation by their incorporation into and shielding by the matrix of the deformable metal. The composite particles also combine the advantages of a coarse powder, including storage with minimum contamination, ease of out-gassing for canned extrusion, non-pyrophoric properties, good flow characteristics and high apparent density, with an extremely intimate and fine dispersion of the constituents in each particle.

Consolidation of the composite powder to metal products may be effected by any suitable process of mechanical working, including extrusion in a sealed can, forging, rolling and hot pressing. The working temperature will, of course, depend on the nature of the composition concerned. During the heating of the particles to the temperature used for working, any homogenisation and annealing of the particles which can occur will generally take place, but further heat-treatment may be performed subsequently if desired. It is generally desirable to de-gas the powder as far as practical before working is carried out.

Some of the various types of wrought products of the invention will now be considered in more detail.

#### Superalloys

Complex nickel, cobalt or iron-base high-temperature alloys (commonly called superalloys) that contain chromium and are rendered age-hardenable by such alloying elements as niobium, titanium and aluminium and/or are solid-solution hardened by molybdenum or tungsten, tend to suffer from segregation on casting, particularly at high contents of the alloying element. This leads to a non-uniform age-hardening response and to hot-working difficulties. If powder metallurgy techniques or blending of elemental or partially pre-alloyed powders is resorted to, it is found that chro-

mium tends to be oxidised and aluminium and titanium tend to be lost by oxidation, so that they are no longer available for age-hardening, and other disadvantages such as segregation also occurs that have already been mentioned.

Further difficulties arose in the attempt to apply dispersion-strengthening to superalloys owing to the ready formation of stringers of dispersoid, resulting in substantial areas within the alloy which were depleted of dispersoid. Manufacture of superalloys by consolidation of wrought composite powders according to the invention facilitates the avoidance of segregation in standard superalloy compositions; enables the content of alloying elements for age-hardening or solid solution hardening to be increased; and enables dispersion-strengthened superalloys to be readily produced. The resulting wrought products have a microstructure that is substantially uniform throughout, are substantially free from segregation, primary gamma prime phase and stringers, and have a uniform distribution of precipitation-hardening phases as indicated by transmission photomicrographs. They may be dispersion-strengthened by any of the wide variety of refractory oxides, carbides, nitrides and borides disclosed in more detail hereinbefore.

It has been noted, quite surprisingly, that bodies produced by hot working of consolidated mechanically alloyed powders can be worked to a much greater extent than conventionally produced bodies of the same composition as the matrix alloy. This is seen in reduced temperatures required for comparable amounts of hot deformation, reduced working pressures and greater permissible amounts of working strain.

Broadly speaking, the alloys have a melting point of at least 1093°C. and contain from 4 to 65 percent by weight of chromium, at least 1% in total of one or more of niobium, aluminium and titanium, preferably 0.2% to 15% aluminium (e.g., 0.5% to 6.5%), and 0.2% to 25% titanium (e.g., 0.5% to 6.5%), 0 to 40% molybdenum, 0 to 40% tungsten, 0 to 20% niobium, 0 to 30% tantalum, 0 to 2% vanadium, up to 15% manganese, up to 2% carbon, up to 1% silicon, up to 1% boron, up to 2% zirconium, and up to 0.5% magnesium, the balance (at least 25%) being essentially iron, nickel, or cobalt with or without dispersion-strengthening constituents, such as yttria, lanthana, alumina, thoria, etc., in amounts from 0.05% to 10% and preferably 0.05% to 10% by volume of the total composition.

Superalloys with which the invention is particularly concerned include those falling within the range 5 to 35% chromium, 0.5% to 8% aluminium, 0.5% to 10% titanium, up to 12% molybdenum, up to 20% tungsten, up to 8% niobium, up to 10% tantalum, up to 2% vanadium, up to 2% manganese, up to 1% carbon, up to 1.5% silicon, up to 0.1% boron, up to 1% zirconium, up to 2% hafnium, up to 0.3% magnesium, up to 45% iron, up to 10% by volume of a dispersoid which is advantageously thoria, yttria, lanthana, ceria, or rare earth oxide mixtures, such as didymia, may suitably be present in amounts of at least 0.2%, preferably 0.5 to 5% by volume, the balance (at least 40%) being one or both of nickel and cobalt. Some specific examples of superalloy compositions which may be produced with or without a dispersoid are set forth in Table I.

TABLE I

Alloy No.	Nominal Composition Wt%														
	C	Mn	Si	Cr	Ni	Co	Mo	W	Cb	Fe	Ti	Al	B	Zr	Other
1	0.12	—	—	12.5	bal.	—	4.2	—	2.0	—	0.8	6.1	0.012	0.10	—
2	0.10	—	—	8.0	bal.	10.0	6.0	—	—	—	1.0	6.0	0.015	0.10	4.0 Ta
3	0.15	—	—	15.5	bal.	—	5.0	—	—	4.5	2.5	3.5	0.05	—	—
4	0.12	0.10	0.30	15.0	bal.	28.5	3.7	—	—	0.7	2.2	3.0	—	—	—
5	0.04	0.55	0.20	15.0	bal.	—	—	—	—	6.5	2.4	0.6	—	—	—
6	0.18	—	—	10.0	bal.	15.0	3.0	—	—	—	4.7	5.5	0.014	0.06	1.0 V
7	0.09	—	—	19.0	bal.	11.0	10.0	—	—	—	3.1	1.5	0.005	—	—
8	0.07	—	—	19.0	bal.	19.0	4.2	—	—	—	3.0	3.0	0.007	0.05	—
9	0.38	1.20	0.40	20.0	20.0	bal.	4.0	4.0	4.0	4.0	—	—	—	—	—
10	0.45	0.25	0.25	21.0	—	bal.	—	11.0	2.0	2.0	—	—	—	—	—
11	0.05	0.10	0.10	12.5	42.5	—	5.7	—	—	bal.	2.8	0.2	0.015	—	—
12	0.04	0.90	0.80	13.5	26.0	—	2.7	—	—	bal.	1.7	0.1	0.005	—	—
13	0.15	1.50	0.50	21.0	20.0	20.0	3.0	2.5	1.0	bal.	—	—	—	—	0.15 N
14	0.05	0.25	0.25	21.5	61.0	—	9.0	—	3.65	25.0	0.2	0.2	—	—	—
15	0.05	—	—	25.0	—	—	10.0	—	—	—	—	—	—	—	0.015 Mg, 0.013 Ce
16	0.1	—	—	15.0	bal.	15.0	4.0	—	—	—	4.0	5.0	—	—	—

The stable refractory compound particles may be maintained as fine as possible, for example, below 0.5 microns in size. A particle size range recognized as being particularly useful in the production of dispersion-strengthened systems is 10 Angstroms to 1,000 Angstroms (0.001 to 0.1 micron).

The heavy cold work imparted to the composite metal particles produced by milling the high-melting metals to produce superalloy compositions is particularly advantageous. It increases effective diffusion coefficients in the product powder and this factor, along with the intimate mixture in the product powder of metal fragments from the initial components to provide small interdiffusion distances, promotes rapid homogenisation and alloying of the product powder upon heating to homogenising temperatures and improves hot workability as explained hereinbefore. The foregoing factors are of particular value in the production of powder metallurgy articles having rather complex alloy matrices. Some examples will now be given:

#### EXAMPLE I

A powder mixture consisting, by weight, of 14.9% of a powdered Ni-Ti-Al master alloy containing Ni 72.93%, Ti 16.72%, Al 7.75%, Fe 1.55%, Cu 0.62%, C 0.033%, Al<sub>2</sub>O<sub>3</sub> 0.05%, TiO<sub>2</sub> 0.036%; 62.25% of carbonyl nickel powder of particle size 5–7 microns; 19.8% of chromium powder of particle size less than 74 microns; and 3.05% of thoria of particle size 0.04 micron, was preblended and 1,300 g. of it was dry impact milled under argon for 48 hours in an attritor mill at a ball-to-powder ratio of 17:1, running at 176 r.p.m. The product consisted of composite powder particles exhibiting excellent inter-dispersion of the ingredients within the individual particles and having a striated structure under a magnification of  $\times 750$ . The analysis of the powder was Ni 73.86%, Cr 19.3%, Ti 2.16%, Al 1.19%, C 0.017%, Cu less than 0.05%, ThO<sub>2</sub> 2.93%, Al<sub>2</sub>O<sub>3</sub> 0.015%, TiO<sub>2</sub> 0.013%. The amount of other impurities was negligible.

After removal of some coarse particles larger than 350 microns, the powder having a particle size range of 45 to 350 microns was extruded to bar in a stainless steel can after degassing under vacuum ( $2 \times 10^{-5}$  mm Hg) at 350°C. using an extrusion ratio of 16:1 and a temperature of 1,175°C. The extruded bar contained a fine and uniform dispersion of thoria particles of average size 0.04 micron with an inter-particle spacing of less than 1 micron, free from stringers, and had a hardness of 275 Vickers. Solution-heating for 16 hours at

1,200°C. reduced the hardness to 235 Vickers, while subsequent aging for 16 hours at 705°C. brought about precipitation-hardening, the hardness increasing to 356 Vickers.

By comparison, wrought alloys having substantially the same matrix composition, produced by conventional melting techniques, had a hardness of 200–250 Vickers after annealing, which was raised to 290–320 Vickers by a similar aging treatment.

#### EXAMPLE II

A mixture consisting, by weight, of 39.5% of a powdered master alloy of particle size less than 43 microns and containing 67.69% Ni, 8.95% Mo, 5.70% Nb, 15.44% Al, 1.77% Ti, 0.053% C, 0.06% Zr and 0.01% B; 45.74% of carbonyl nickel powder of particle size 5 microns; 11.64% of chromium powder of particle size less than 74 microns; and 3.12% of thoria of particle size 0.04 microns, was dry milled for 48 hours in air in an attritor mill at a ball-to-powder ratio of 29:1 by volume and a speed of 176 r.p.m. Microscopic examination of the powder revealed that the constituents had intimately united together to form composite metal powder particles which showed excellent inter-dispersion of the ingredients.

A portion of the powder product, after removal of coarse particles larger than 350 microns was extruded to bar in a stainless steel can (after degassing under vacuum at 425°C.), using an extrusion ratio of 16:1 and a temperature of 1,200°C. The resulting bar had the analysed composition: C 0.07%, Cr 10.40%, Mo 3.00%, Nb 1.60%, Al 5.20%, Ti 0.65%, B 0.007%, Zr 0.03%, ThO<sub>2</sub> 3.20%, Al<sub>2</sub>O<sub>3</sub> 0.38%, TiO<sub>2</sub> 0.018%, Cr<sub>2</sub>O<sub>3</sub> 0.016%, Ni balance. The Al<sub>2</sub>O<sub>3</sub> was present as an intimate dispersion and the proportion of the extraneous oxides, TiO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> was thus very low.

Portions of the extruded bar were heated to 1,240°C. for 4 hours in argon to solution-treat the alloy, increase its grain size and complete the homogenisation of the structure, and then furnace-cooled to allow precipitation-hardening to occur. The grain structure of the alloy after this treatment is shown at a magnification of  $\times 100$  in FIG. 2 of the drawings. It will be noted that the grain structure is elongated in the direction of extrusion. On examination by electron microscopy after this treatment the alloy was observed to contain both a gamma prime precipitation-hardening phase and an intimate dispersion of thoria particles of average size 0.05 micron, with an inter-particle spacing of less than 1 micron. The fine structure under the electron micro-

scope at 10,000 diameters is shown in FIG. 3 of the drawings.

The high-temperature properties of the alloy after heat-treatment are set forth in Table II.

TABLE II

Test Temp. (°C.)	Yield Strength 0.2% offset (kg/mm <sup>2</sup> )	Tensile Strength (kg/mm <sup>2</sup> )	Elongation %	R.A. %
760	69.6	79.0	7.5	10.0
982	19.3	24.9	11.0	8.0
1093	7.5	8.2	9.0	24.5

The improvement brought about by the dispersion of thorium in the alloy is shown by comparison of the stress-rupture properties of the heat-treated alloy with those of a cast, precipitation-hardened high-temperature alloy (Alloy 713) containing no thorium and having a composition similar to that of the matrix of the thorium-containing alloy, namely Ni 74.84%, Cr 12.0%, Mo 4.5%, Nb 2.0%, Ti 0.6%, Al 5.9%, C 0.05%, Zr 0.1%, B 0.01%. These properties are compared in Table III in terms of the stress at which the alloys exhibited lives of 100 and 1,000 hours at 1,093°C.

TABLE III

Life Hours	Stress for indicated life (kg/mm <sup>2</sup> ) ThO <sub>2</sub> -containing alloy	Alloy 713
100	6.0	4.5
1000	5.4	2.9

## EXAMPLE III

An 8.5 kg. powder charge of 1,550 parts of a nickel master alloy containing 7% aluminium, 14% titanium and 9% didymium (a rare earth metal mixture containing 50% lanthanum with neodymium and praseodymium and other rare earth metals) ground to pass a 74 micron screen; 1,800 parts of chromium powder smaller than 74 microns; 20.4 parts of Ni-Zr master alloy, 3.87 parts of Ni-B master alloy; and 5,241 parts of carbonyl nickel powder was dry impact milled in a 38 litre attritor mill containing 189 kg. of 6.3 mm. nickel pellets for 40 hours at an agitator speed of 132 r.p.m. The product was screened through a 350 micron sieve and packed into an 8.9 cm. diameter steel can, which was sealed without evacuation, soaked at 1,038°C. and extruded to round bar 1.9 cm. diameter. The powder became consolidated by upsetting within the container prior to extrusion and good hot workability was evident from the fact that extrusion was possible at the relatively low temperature of 1,038°C. The extruded bar was subjected to heat treatment comprising heating 2 hours at 1,275°C. followed by heating 7 hours at 1,080°C. and then for 16 hours at 705°C. A coarse grain structure elongated in the extrusion direction was present. The extruded bar was characterized by a finely-divided and well-distributed dispersion of rare earth metal oxides, principally lanthana resulting from internal oxidation by reaction of extremely finely-divided rare earth metal and oxygen present in the milled powder.

The stress rupture properties of the heat treated bar were very good as illustrated by data set forth in the following Table IV, indicating a very uniform dispersion of fine refractory oxide particles.

TABLE IV

Test Temp. (°C)	Stress (kg/mm <sup>2</sup> )	Time to rupture (Hrs.)	Elongation (%)	Reduction in area
1038	12.7	1.5	8.0	11.6
1038	11.2	472.7	4.0	6.0
1038	9.8	389.7	2.7	3.9
760	35.2	16.3	2.7	3.9
760	28.1	193.1	4.4	7.0

This example illustrates a special feature of the invention whereby dispersion-strengthened metals may be produced using as a starting material a powder having distributed therethrough on a micro-scale a metal whose oxide has a high heat of formation at 25°C. exceeding 90 kg. cal. per gram atom of oxygen. Said metal becomes oxidized in situ by oxygen available in limited supply in the powder by virtue of the very short diffusion distances involved, with the result that the resulting oxide is very fine and is well distributed in the resulting consolidated shape wherein the oxide is an effective dispersion strengthener.

## EXAMPLE IV

A further 8.5 kilogram powder charge containing about 1,490 parts of a Ni-17%, Ti-8.5%, Al master alloy ground to less than 75 microns, 2,000 parts of chromium smaller than 75 microns, 1,330 parts of fine carbonyl nickel powders premixed with 10%, by weight, of fine yttria (400 A) in a Waring blender, 24.8 parts of a Ni-Zr master alloy smaller than 75 microns, 3.9 parts of a Ni-B master alloy smaller than 75 microns and 5,290 parts of carbonyl Ni powder was milled for 40 hours in a 38 litre attritor mill containing 180 kg of 6.3 mm. nickel pellets at 132 r.p.m. The product powder was screened through a 350 micron screen and packed into a 8.9 cm. diameter steel can. The can was evacuated to less than 10<sup>-4</sup> mm. of mercury pressure at 425°C. and sealed by welding. The sealed, evacuated can was heated to 1,093°C. and extruded to 15.5 mm. diameter bar. The extruded bar was heated in argon 2 hours at 1,275°C., then at 1,080°C. for 7 hours and cooled in air. It was then heated for 16 hours at 705°C. and again air cooled. A desirable coarse grain 2.46 elongated in the extrusion direction resulted. The bar contained 0.061% C, 0.92% soluble Al, 2.46% soluble Ti, 20.4% Cr, 0.029% soluble Zr, 0.005% B, 1.22% Y<sub>2</sub>O<sub>3</sub> and 0.37% Al<sub>2</sub>O<sub>3</sub>.

Specimens of the extruded, heat treated bar were subjected to stress-rupture testing with the excellent results set forth in the following Table V.

TABLE V

Temp. (°C.)	Stress (kg/mm <sup>2</sup> )	Life to rupture (hrs.)	Elongation (%)	Reduction in area (%)
1038	12.7	5.8	3.2	9.0
1038	11.5	70.9	4.0	9.4
1038	11.2	393.6	2.7	1.6
927	17.6	7.1	6.2	10.5
927	15.8	117.4	5.3	11.6
760	35.2	4.0	7.2	20.5
760	28.1	131.3	6.4	21.5
760	28.1	53.3	10.0	19.1

In addition, the yttriated material was found to be markedly more resistant to sulfidation corrosion result-

ing from exposure at 927°C. to a fused salt bath containing, by weight, 90% sodium sulfate and 10% sodium chloride than the non-dispersion strengthened base alloy. Similarly, the yttriated material was markedly more resistant than the non-dispersion strengthened base alloy in a cyclic oxidation test at 1,093°C. in flowing air wherein the specimens were cycled to room temperature every 24 hours. In particular, the yttriated material was much more resistant to subsurface penetration than was the standard material in these tests.

FIG. 4 is a transmission electron photomicrograph taken at 100,000 diameters from the yttriated material of this example. The fine, substantially uniform distribution of finely divided dispersoid (yttria and alumina) as indicated by reference character G, and a substantially uniform distribution of gamma prime phase as indicated by reference character H in FIG. 4. Somewhat larger MC metal carbides indicated by reference character J are also evident in FIG. 4. FIG. 4 demonstrates the absence of segregation which characterizes materials of this invention.

#### EXAMPLE V

Composite alloy powders having the composition of a conventional nickel base superalloy containing 10% Cr, 3% Mo, 15% Co, 5.5% Al, 4.7% Ti, 1% V, 0.18% C, 0.06% Zr, 0.014% B, balance Ni, were produced by mechanical alloying. A mixture of 441 g. of Cr powder (less than 150 microns), 134 g. of Mo powder (less than 44 microns), 663 g. of Co powder (less than 44 microns), 1,005 g. of carbonyl Ni powder, 7.6 g. of graphite powder, 1,050 g. of less than 75 micron powder of a Ni-15.96% Al-3.68% Ti master alloy, 932 g. of less than 75 micron powder of a Ni-9.08% Al-17.5% Ti master alloy, 71 g. of a less than 150 micron powder of a Ni-65% V master alloy, 12 g. of a less than 75 micron powder of a Ni-28% Zr- 14.5% Al master alloy and 3.3 g. of a less than 75 micron powder of a Ni-18% B master alloy were placed in a high energy horizontal ball mill of 15 litres capacity having a stationary tank and a driven horizontal shaft provided with multiple agitator arms extending at right angle therefrom, and processed at 220 r.p.m. with 90 kg. of 9.5 mm. steel balls. A nitrogen atmosphere was maintained in the mill. Two batches were processed for 16 hours, one for 8 hours and one for 4 hours.

The internal powder structure of the batches processed for 16 hours was observed to be substantially homogeneous with the majority of the ingredient fragments within the composite particles being below 1 micron in size. In contrast, the structures of the 8 hour and 4 hour batches were progressively less homogeneous although all had substantially the same overall composite particle size distributions.

3,066 g. of one of the 16 hour batches, sieved to pass through a 350 micron screen was packed in a 8.9 cm. diameter mild steel can and evacuated to less than  $10^{-4}$  mm of mercury pressure at 425°C. through a stainless steel tube provided for that purpose. The can was sealed by fusion welding the tube and consolidated by hot extruding to 2.5 cm. diameter bar at 1,177°C. The extrusion was accomplished with no difficulty, requiring less than two-thirds of the capacity of the press and moving at a ram speed of from 33 to 61 cm. per second. This, in spite of the fact that the composition as normally produced, is not readily hot workable and must be precision cast to final shape.

The results of hardness tests performed on samples of this extrusion in the as extruded condition and after two annealing treatments are given in Table VI.

TABLE VI

Condition	Hardness Rc
As extruded	48
2 hours at 1243°C.	42.5
2 hours at 1266°C.	40.5

#### Wrought, Dispersion-Strengthened Electrical Heating Elements

Heat-resistant alloys for electrical heating elements, comprising one or both of iron and nickel alloyed with one or both of chromium and aluminium, suffer from segregation when made by casting. Soaking to homogenise the structure leads to little improvement and may result in grain coarsening, with adverse effects on forgeability, extrusion and rolling. In particular, certain well-known alloys which contain both aluminium and chromium, together with nickel or iron or both, are brittle at room temperature although soft at elevated temperatures. One such alloy contains 67% iron, 25% chromium, 5% aluminium and 3% cobalt and another 55% iron, 37.5% chromium and 7.5% aluminium. These two alloys exhibit excellent resistance to oxidation and corrosion at elevated operating temperatures of about 1,200–1,300°C., but tend to creep and lose their shape during service as electrical resistance elements.

These disadvantages are overcome by the wrought, dispersion-hardened electrical heating alloys provided by the invention which are characterized throughout by compositional uniformity (i.e., freedom from segregates) and by a high degree of dispersion uniformity and absence of stringers and attendant dispersoid free regions.

Broadly speaking, the alloys concerned are those containing at least 10% in all of one or both of chromium and aluminium, the chromium content not exceeding 40% and the aluminium content not exceeding 34%, and from 0 to 5% silicon, the balance of the alloy (apart from impurities) being at least 50% in all of one or more of iron (5% to 75%), cobalt (up to 15%) and nickel (5% to 80%), and including from 0.05% to 25% by volume (based on the total composition) of a refractory compound dispersoid. Generally, the alloys have an electrical resistance of at least 100 microhms/cm<sup>2</sup>.

Advantageously, the chromium content is from 15 to 40%, the cobalt content does not exceed 10%, the aluminium content does not exceed 32%, the sum of the iron, cobalt and nickel content is from 50 to 80% and the dispersoid content is from 0.05 to 10 volume percent of the total composition.

A composition range particularly desirable for electrical heating alloys contains 15–40% chromium, 3–20% aluminium, balance iron, with from 0.05 to 5 volume percent of dispersoid.

Dispersoids that are particularly useful are yttria, lanthana, thoria and the rare earth mixture didymium, in sizes less than 1 micron and preferably less than 0.1 micron. Oxides of zirconium, titanium, and beryllium and carbides, nitrides and borides of all the metals set forth above may also be used. Generally speaking, suitable

refractory oxides are those of metals whose negative free energy of formation of the oxide per gram atom of oxygen at 25°C. is at least 90,000 calories and whose melting point is at least 1,300°C.

Specific examples of alloys that may be dispersion-strengthened by the invention are set forth in Table VII below:

TABLE VII

Alloy No.	Resistance Microhms/cm <sup>3</sup> at 20°C.	Nominal Composition				
		% Cr	% Al	% Fe	% Ni	% Others
17	1387	23	5	72	—	—
18	1662	37.5	7.5	55	—	—
19	1379	20	5	73.5	—	1.5 Si
20	1163	20	—	8.5	68	2 Si
21	1122	16	—	22.5	60	1.5 Si
22	—	25	5	67	—	3 Co
23	—	15	5	—	80	—
24	—	20	4	—	76	—
25	—	15	5	5	75	—
26	—	—	15	Bal.	—	—
27	1013	20	—	43.5	35	1.5 Si
28	—	—	31.5	—	68.5	—
29	—	20	—	—	80	—

Some examples will now be given:

## EXAMPLE VI

An iron-aluminium alloy dispersion-strengthened with Al<sub>2</sub>O<sub>3</sub> is made from composite powder produced by dry impact milling a charge of 65 micron sponge iron and an Fe-Al master alloy crushed to powder smaller than 74 microns in the appropriate proportions with 3 volume percent of 0.03 micron gamma alumina using a 20:1 ball-to-powder ratio and 6 mm. nickel balls and an agitator speed of 175 r.p.m. Milling for 45 hours produced a highly cold-worked powder of which the particles comprised a substantially homogeneous interdispersion of all the ingredients. The powder was vacuum packed in a mild steel can which was welded shut, heated to 1,093°C. and extruded at a ratio of 16:1. After removal of the can material, the extruded bar was hot- and cold-worked to ribbon and wire for use as electrical heating elements.

## EXAMPLE VII

In producing a wrought dispersion-strengthened electrical heating alloy containing, by weight, 20% Cr, 5% Al, 1.5% Si and 73.5% iron with 4 volume percent of Y<sub>2</sub>O<sub>3</sub>, 2,300 g. of a brittle master alloy containing, by weight, 63.25% Fe, 21.7% Al, 6.5% Si and 8.55% yttrium metal, crushed to particles smaller than 75 microns, was blended with 4,870 g. of 150 micron high-purity sponge iron and 2,830 g. of 75 micron ferrochrome powder. The mixture was dry impact milled in a stirred attritor mill of 38 litres capacity at 180 r.p.m. using 6 mm. hardened steel balls at a ball:powder ratio of 15:1. Milling for 24 hours gave fully work-hardened composite powder. After sieving out particles larger than 0.35 mm., the powder was vacuum packed and welded shut in a mild steel can and the assembly heated to 1,093°C. During this heating the oxygen adventitiously present within the powders combined with the yttrium metal to produce a fine uniform dispersion of Y<sub>2</sub>O<sub>3</sub> of less than 0.1 micron average particle size. The can was then extruded at 1,093°C. at an extrusion ratio of 16:1 to rod, suitable for drawing down to size suitable for electrical heating elements.

## EXAMPLE VIII

To produce a ThO<sub>2</sub> dispersion-strengthened electrical heating alloy containing Cr 15%, Al 5%, Fe 5% and Ni 75%, a brittle master alloy containing Al 67%, Fe balance was crushed to particles smaller than 150 microns. 89.5 g. of the crushed powder was blended was 68.3 g. of a commercial Cr 70%-Fe 30% powder of par-

25 ticle size less than 150 microns, 132.2 g. of Cr powder of particle size less than 75 microns, 900 g. of 5-7 micron Fisher size carbonyl Ni powder, and sufficient 0.02 micron ThO<sub>2</sub> to give 3 volume percent ThO<sub>2</sub> in the product. The mixture was dry impact milled for 50 hours at 185 r.p.m. in a stirred attritor mill of 3.8 litres capacity using 6 mm. nickel balls at a ball:powder ratio of 18:1. The composite powder was sieved through a 0.35 mm. mesh screen and vacuum packed and welded shut in a mild steel can; heated to 1,093°C; and extruded at a ratio of 15:1 to rectangular section rod. The rod had ThO<sub>2</sub> particles less than 0.02 micron in size uniformly dispersed through it, which conferred stiffness and resistance to sagging in use at elevated temperatures.

40 Other dispersion-strengthened products that can advantageously be made include dispersion-strengthened nickel, copper, low alloy steels, maraging steels, zinc-base alloys, the refractory metals chromium, niobium, tantalum, molybdenum and tungsten and their alloys, e.g., with up to 50% of other metal, platinum metal-base alloys and gold-base alloys. Some examples of these will now be given.

## Dispersion-Strengthened Nickel

## EXAMPLE IX

50 A charge consisting of 1,173 g. of carbonyl nickel powder having an average particle size of 3 to 5 microns and 27 g. of thoria having a particle size of 0.005 micron was preblended in a high speed food blender and then dry impact milled in air at room temperature for 24 hours. The mill contained 3.8 litres of carbonyl nickel balls of average diameter 6.2 mm., the ball-to-powder ratio being 18:1 by volume, and was operated at an agitator speed of 176 r.p.m., which served to maintain substantially all the balls in a highly active state of mutual collision in which the ratio of the powders to the dynamic interstitial volume was about 1:18 by volume. The milled product consisted of composite particles of nickel with thoria particles very finely and uniformly disseminated through them, and having saturation hardness of 640 to 650 Vickers. After removal of the few coarse particles, the powder was placed in

a mild steel extrusion can, degassed under vacuum at 400°C., and then sealed in the can and extruded to bar at 982°C. at an extrusion ratio of 16:1. The extruded product consisted of a nickel matrix with grain size less than 5 microns having a fine, stable, substantially uniform dispersion of thoria particles less than 0.2 micron and most about 0.02 micron in size.

The properties of the material in the as-extruded condition and after various amounts of cold swaging are given in the following table:

TABLE VIII

Test Temp. °C.	Hot Ultimate Tensile Strength (kg/mm <sup>2</sup> ) % R.A.			
	As-extruded	40%	61%	75%
760	13.1	—	—	26.2
982	7.4	11.5	15.4	18.5
1093	5.3	—	—	14.7

R.A. = Reduction in area

It will be observed that this very satisfactory structure in the extruded material, and the associated high level of properties, were obtained from the composite powder of the invention with an extrusion ratio of only 16:1.

## EXAMPLE X

Batches of composite nickel-thoria powder were prepared by dry impact milling charges of 777.4 g. of carbonyl nickel powder and 22.6 g. of thoria, particle size 100–500 Angstroms, preblended in a high speed blender, for 24 hours in air at room temperature in the attritor mill of Example IX, using carbonyl nickel balls of average diameter 4.5 mm. at a ball-to-powder ratio of 26:1. The agitator speed was 176 r.p.m. After combining several batches of the product powder and removal of particles too large to pass a 0.35 mm. mesh screen, 2,500 g. of the composite powder were sealed in an 8.9 cm. diameter mild steel can and extruded to 2.2 cm. diameter bar at 982°C. Stress rupture tests at 1,093°C. on specimens of the bar that had been further cold swaged to 75% reduction in area gave the following results:

TABLE IX

Stress (kgf/mm <sup>2</sup> )	Life (hours)	Elongation (%)
9.14	4.3	—
8.44	12.5	2.5
7.74	120.1	5.0

## EXAMPLE XI

The strength of a 90% tantalum — 10% tungsten alloy is increased by the incorporation of thoria. A mixture of 2,160 g. tantalum and 240 g. tungsten, particle size from 3 to 40 microns, with 28 g. of 0.02 micron ThO<sub>2</sub> (about 2% by volume) was preblended and then dry impact milled in a nitrogen atmosphere for 40–50 hours at 176 r.p.m., using 1 cm diameter hardened steel shot at a ball:powder ratio of 2:1 in an attritor mill as described in Example IX. After 48 hours the powder product had reached saturation hardness. After screening out particles larger than 0.35 mm, the composite powder was placed in an 8.9 cm. diameter molybde-

num can, which was evacuated, sealed and extruded to 2 cm. diameter at 1,315°C. The dispersion of thoria in the resulting wrought bar was highly uniform both longitudinally and transversely.

## EXAMPLE XII

In producing dispersion-strengthened niobium, 1,100 g. of 10–50 micron Nb powder was preblended with 26 g. of 0.04 micron thoria powder, and dry attritor milled in a nitrogen atmosphere at 176 r.p.m. for 48 hours using 6 mm. tool steel balls at a ball:powder ratio of 18:1. After sieving through a 0.35 mm. screen, the composite powder was charged into an 8.9 cm. molybdenum can which was evacuated, sealed, heated to 1,482°C. in hydrogen, and extruded into 2.5 cm. bar at 1,482°C.

## EXAMPLE XIII

Dispersion-hardened tungsten was produced by milling a charge of 2,500 g. of W powder with 27 g. ThO<sub>2</sub> (2% by volume) as in the preceding example, to give a composite powder which was screened and extruded in an 8.9 cm. evacuated Mo can, after heating to 1,925°C. in hydrogen, to bar 2.5 cm. in diameter.

## Dispersion-Strengthened Low-Alloy Steels

Dispersion-strengthening of low-alloy steels, particularly those containing molybdenum or vanadium, with or without chromium, having for example, the composition set out in the following Table, enables low alloy steels having improved high temperature tensile and creep strength to be produced.

Low alloy steels which may be produced in accordance with the invention include steels containing up to 0.8% carbon, at least 0.25% of one or both of Cr up to 5% and Mo up to 5%, from 0 to 2% V, from 0 to 2% W, from 0 to 5% Ni, from 0 to 2% Si, and from 0 to 2% Mn. Examples of such steels are given in the following Table X:

TABLE X

Alloy Steel No.	% C	Nominal Composition By Weight			
		% Cr	% Mo	% Fe	% Others
1	0.08	5	0.5	bal.	0.5 Ti
2	0.12	5	0.5	bal.	1.2 Si
3	0.15	—	0.5	bal.	—
4	0.17	0.5	0.5	bal.	—
5	0.12	1	0.5	bal.	—
6	0.13	0.6	0.01	bal.	0.65 Mn 0.018 P
7	0.08	1.25	0.5	bal.	0.06 Zr
8	0.13	2	1.0	bal.	—
9	0.12	2.25	0.5	bal.	—
10	0.4	2	0.35	bal.	—
11	0.4	1	—	bal.	0.25 V

## EXAMPLE XIV

In producing a dispersion-strengthened low alloy steel containing 2% Cr, 1% Mo and 0.4% C, a brittle master alloy containing 30% Cr, 15% Mo, 5% C, balance Fe was ground to pass a 74 micron screen, and 80 g. were preblended with 1,120 g. of 65 micron sponge iron. This mixture was dry milled with 30 g. of 0.02 micron ThO<sub>2</sub> as in the preceding Example. After screening through a 0.35 mm. screen, the composite powder was placed in an 8.9 cm. mild steel can which was heated to 400°C., evacuated, quenched under vacuum,

sealed and extruded at 982°C. to 2 cm. diameter rod.

#### Dispersion-Strengthened Maraging Steel

The recently developed maraging steels, i.e., steels that are age-hardenable in the martensitic state and have compositions broadly within the range Ni 10–30%, Ti 0.2–9% and Al up to 5%, such that (Ti + Al) does not exceed 9%, Co up to 25%, Mo up to 10%, Fe balance (at least 50%) would benefit from dispersion strengthening. The rather sluggish diffusivity of molybdenum and other materials in powder mixtures may be countered by the use of composite powders in the present invention. Incorporation of a dispersoid in the powder enables a dispersion-strengthened product to be made by hot extrusion that has improved strength properties in the range 480–650°C.

#### Dispersion-Strengthened Zinc-Base Metals

Wrought zinc and zinc alloys, containing, for example, 50% or more zinc, can be dispersion-strengthened in accordance with the invention, thus increasing their resistance to creep. Examples of such alloys include: Pb 0.15–0.35%, Cd 0.15–30%, Zn bal.; Pb 0.005–0.1%, Cu 0.5–1.5%, Ti 0.12–1.5%, Zn bal.; Mg up to 0.025%, Al 0.25–0.6%, Zn bal.; Cu up to 3.5%, Mg 0.02–0.1%, Al 3.5–4.5%, Zn bal.

#### EXAMPLE XV

In producing dispersion-strengthened zinc, 1,500 g. of Zn powder that passes a 150 micron screen was preblended with 25 g. of 0.02 micron gamma alumina and dry impact milled for 50 hours at 180 r.p.m. using a 20:1 ball: powder ratio of hardened steel balls. After sieving to remove coarse particles larger than 0.35 mm., the composite powder was cold-pressed to a 6.3 cm. diameter cylinder, which was sintered for 3 hours at 315°C. in very dry hydrogen. The sintered billet was machined smooth and consolidated by extrusion at 177°C. to a 1.6 cm. diameter rod that had a highly uniform dispersion of Al<sub>2</sub>O<sub>3</sub> particles in both the longitudinal and transverse directions and was substantially free from stringers.

#### Dispersion-Strengthened Platinum Group Metals and Alloys

Dispersion-strengthening of platinum-base metals is particularly desirable to improve their strength at elevated temperatures, and alloys that can advantageously be strengthened include Pt with up to 50% Pd; Pt with 3.5–40% Rh; Pt with up to 35% Ir; Pt with up to 8% W. Examples of dispersion-strengthened Pt-base metals that can be produced as wrought shapes in accordance with the invention are: Pt with 2 vol. % of 0.02 micron ThO<sub>2</sub>; Pt 75%-Rh 25% with 3 vol. % of 0.04 micron yttria; Pt 92%-W 8% with 5 vol.% of 1 micron Ti carbide; Pt 90%-Pd 10% with 2 vol.% of 0.1 micron ZrO<sub>2</sub>.

#### Dispersion-Strengthened Gold-Base Metals

Gold is quite soft and has low resistance to creep. It can be hardened by addition of alloying elements, and this method of hardening can be replaced or supplemented by dispersion-hardening in accordance with the invention. Gold-based metals that can be advantageously so hardened include gold alloys, e.g., Au 54–60%, Pt 14–18%, Pd 1–8%, Ag 7–11%, Cu 7–13%, Ni 1% max., Zn 1% max.; Au 62–64%, Pt 7–13%, Pd 6% max., Ag 9–16%, Cu 7–14%, Zn 2% max., and Au 70%–Pt 30%. Volume loadings of up to 10% or more of dispersoids such as thoria, yttria, alumina and refrac-

tory carbides can readily be produced in wrought gold-base metals.

#### Dispersion-Strengthened Copper

An example of the dispersion-strengthening of copper to improve its resistance to creep at elevated temperatures while maintaining high electrical and thermal conductivity is as follows:

#### EXAMPLE XVI

A charge of 1,173 g. of 7–10 micron Fisher sub-sieve size Cu powder and 27 g. of 0.03 micron alumina was dry milled for 30 hours at 176 r.p.m. in the stirred attritor mill of FIG. 1, using 6.5 mm. hardened steel balls, the ball:powder ratio being 18:1. The composite powder (after screening) was compacted and sintered in hydrogen at 850°C. for 1 hour, then vacuum welded into a Cu can and hot extruded at a ratio of 18:1 at 800°C. to produce a wrought Cu product substantially free from stringers. The product after reduction to wire had high electrical and thermal conductivities together with strength at both ambient and elevated temperatures substantially above that of pure copper.

#### Sintered Refractory-Metal Compositions

Sintered refractory-metal materials, such as sintered refractory carbides, otherwise known as cemented carbides, which are widely used for cutting or abrasion-resistant tools, oil drilling bits and dies, consist of 24 percent or more by volume of finely divided particles of the hard refractory compound and embedded in a matrix of iron, nickel, cobalt or other ductile metal to form a body of high hardness and compressive strength. Conventionally, the sintered body is formed by compacting a mixture of the refractory compound, e.g., tungsten carbide, and the matrix-forming bonding metal, in the form of finely-divided powders, and heating the compact in vacuum or dry hydrogen to bring about liquid phase sintering.

The preferred binder metal is cobalt, since this dissolves only about 1% tungsten carbide at ambient temperatures and therefore provides a tough matrix. Iron and nickel dissolve more tungsten carbide and thus form less ductile matrices.

The mixture of tungsten carbide, cobalt, and an organic wax binder is made by milling the powder for 60 hours or more in a protective fluid, such as hexane, containing stainless steel balls. During the milling, part of the cobalt powder is smeared onto the surface of the carbide particles as a very thin coating.

The microstructure of the compounds, in particular the size of the carbide particles in the matrix; their distribution; and the porosity and the quality of the bond between the binder metal and the carbide particles, are factors which affect the hardness and strength of the sintered product. The average particle size of refractory carbides in the sintered product is limited by that of the starting materials, which is generally from 2 to 10 microns.

This difficulty is overcome, and an extremely finely dispersed structure of very fine particles of carbide or other refractory compound is obtained, if the carbide is incorporated into composite particles inter-dispersed with the binder metal by dry impact milling in accordance with U.S. application No. 709,700. These particles are to be distinguished from those resulting from the conventional blending operation, in which the binder metal is smeared onto the hard particles as a coating. According to the invention, sintered refractory

compound materials are made by compacting and sintering composite particles containing finely divided and inter-dispersed constituents in which the distance between the constituent sub-particles is advantageously less than 10 microns and preferably less than 2 microns, or even 1 micron. This may be done in various ways. A body of powder can be consolidated by hot pressing at an elevated temperature high enough for sintering to occur; it can be first hot-compacted or cold-compacted and sintered under non-oxidising conditions; or the mixture may be extruded in a can, e.g., of steel, and the whole extruded at a temperature high enough for sintering to occur during extrusion. The wrought products produced in any of these ways have a high degree of dispersion uniformity of the hard phase in the matrix.

The refractory compound, which comprises 30 percent or more by volume of the composition, may be a carbide, boride or nitride, of titanium, zirconium, hafnium, chromium, tungsten, molybdenum, vanadium, columbium, tantalum; silicon carbide, or an oxide of aluminium, beryllium, a rare earth metal, e.g., cerium, lanthanum, or yttrium, magnesium, zirconium, titanium, and thorium. Intermetallic compounds such as aluminides, beryllides or silicides may be used under conditions in which they retain their identity.

The matrix-forming binding metal may comprise at least one metal from the following groups:

- a. the iron group metals iron, nickel, cobalt; alloys of these metals with each other; and alloys of at least one iron group metal with at least one of the metals chromium, molybdenum, tungsten, niobium, tantalum, vanadium, titanium, zirconium and hafnium.
- b. a metal or alloy of the group silver, copper, and a ductile metal of the platinum group (e.g., platinum, palladium, rhodium or ruthenium).
- c. aluminium, zinc, lead or alloys thereof.

The matrix-forming binding metals of group b are particularly useful in the production of wear resistant electrical contact elements.

The binder alloys of group a include the well known superalloy compositions capable of being age-hardened at temperatures of about 600° to 1,000°C. These resist softening under conditions where the cutting tool is used at relatively high cutting speeds which tend to overheat the cutting edge of the tool. Examples of age-hardenable superalloy compositions are those falling within the following range by weight: 4% to 65% chromium, at least 1% in sum of an age hardening element selected from the group consisting of up to 15% aluminium and up to 25% titanium, up to 40% molybdenum, up to 20% niobium, up to 40% tungsten, up to 30% tantalum, up to 2% vanadium, up to 15% manganese, up to 2% carbon, up to 1% silicon, up to 1% boron, up to 2% zirconium, up to 4% hafnium and up to 0.5% magnesium, the balance essentially at least one element from the group consisting of iron, nickel and cobalt with the sum of these being present in an amount of at least about 25%.

Examples of compositions are as follows:

Co 15-25% with up to 3 wt. percent (TaC + TiC), balance WC;

Co 25-45% with up to 2 wt. percent (TaC + TiC), balance WC;

Co 15-25% with 10-22 wt. percent TiC, balance WC;

Co 15-25% with 18-30% TaC, balance WC;

Ni-Mo alloy 15-50%, TiC 85-50%

The Ni-Mo matrix alloy in the last composition may contain 25-70%, advantageously 35-60% molybdenum, balance nickel.

The compositions also include the recently-developed heat resisting metal carbide compositions for high temperature applications, known as cermets, for example, from 85 to 24 volume percent, and preferably at least 60 percent, of carbides of titanium and chromium with the balance nickel or nickel-base alloy as the binder metal. The carbide phase generally consists predominantly of TiC with up to 25 percent of Cr carbide.

Some examples will now be given:

#### EXAMPLE XVII

A powder mixture of 25% of 5-7 micron Co and 75% of 3-5 micron WC by weight (63 percent WC by volume) is dry impact milled in a stirred attritor mill of the type shown in FIG. 1 at 185 r.p.m., using hardened steel balls at a ball:powder ratio of 25:1 for 50 hours to form a wrought composite powder consisting of particles having WC particles homogeneously inter-dispersed in a Co matrix. The WC particles were reduced in size to less than 1 micron. The powder was consolidated by hot pressing in a graphite die at 1,350°C. for 3 minutes using 35 kg/cm<sup>2</sup> pressure.

#### EXAMPLE XVIII

To produce a heat- and oxidation-resistant TiC/Ni 80-Cr 20 alloy cermet composition, a mixture of 1,240 g. of 5-7 microns TiC particles, 448 g. of 4-8 micron carbonyl Ni and 112 g. of Cr powder smaller than 75 microns was dry impact milled in a stirred attritor mill of the type shown in FIG. 1 at 180 r.p.m. for 50 hours, using 6 mm. hardened steel balls at a ball:powder ratio of 20:1 to produce a wrought composite powder in which the particles comprised uniformly inter-dispersed Ni, Cr and TiC.

#### EXAMPLE XIX

This is an example of the production of a sintered electric contact material containing 50% Ag and 50% WC, by weight, (40% WC by volume).

A composite powder was made by dry milling 1,000 g. of Ag of particle size below 75 microns and 1,000 g. of 5-7 microns WC powder, using an attritor mill containing hardened steel balls at a ball:powder ratio of 18:1, and operating at 185 r.p.m. for 45 hours. The WC particles were reduced by the milling to less than 1 micron in size. The powder is then screened to remove particles coarser than 100 microns and then hot pressed into shapes for electrical contacts in a graphite die by exerting a pressure of 35 kg/cm<sup>2</sup> for three minutes at a temperature slightly above the melting point of silver, e.g., at 980°C.

An example of another composition that can be made by similar techniques is a titanium carbide composition (79 vol.%, 65 wt.% TiC) containing 35% by weight of a 50-50 nickel-molybdenum alloy as binder.

#### Metal Systems of Limited Solubility

Metal systems comprising two or more metal constituents having limited mutual solubility in the liquid and/or the solid state, i.e., that are immiscible or only partly miscible, tend to segregate or separate on solidi-



fication if it is attempted to make them by melting. Infiltration of one molten metal into a solid skeleton of the other, e.g., copper into iron, or compacting mixtures of the respective powders followed by liquid phase sintering, also lead to non-uniform segregated microstructures, subject to the limitations imposed by the particle sizes of the powders employed.

Consolidated metal products of these systems can readily be made from appropriate composite powders by the invention, with a highly refined internal structure substantially free from segregation, lakes, pools or dendritic coring.

Examples of binary systems of limited solubility include: lead-copper, copper-iron, copper-tungsten, silver-tungsten, copper-chromium, silver-chromium, copper-molybdenum, silver-molybdenum, silver-manganese, silver-nickel, platinum-gold, beryllium-molybdenum, and silver-platinum. The invention is also applicable to limited solubility metal systems containing three or more elements, e.g., copper-nickel-chromium.

Examples of composition ranges that may be produced are: Cu with 1-95% Pb; Fe with 1-95% Cu; W with 5-95% Cu; W with 2-98% Ag; and Cu with 5-95% Cr.

#### EXAMPLE XX

This is an example of the production of a composite iron-copper powder containing Fe 80%, Cu 20%.

Hydrogen-reduced copper, particle size less than 45 microns, and sponge iron, particle size less than 150 microns, were dry impact milled in air in a 50 c.c. capacity high speed shaker mill operated at 1,200 cycles per minute, which produced composite metal particles in a very short period of time compared with the attritor mill of FIG. 1. The mill was charged with 10 g. of powder and 45 g. of 6.2 mm. nickle balls to give a ball-to-powder ratio of 4.5:1 and a ratio of dynamic interstitial volume to powder volume of 41:1.

Milling for 30 minutes produced composite particles of hardness of 353 Vickers and average size 135 microns, with a fine, uniform striated structure, the average spacing between striations being about 1 micron.

Consolidation by compacting in a steel tube which was vacuum sealed, followed by hot forging at 982°C. to full density gave a highly uniform wrought product.

#### EXAMPLE XXI

This is an example of the production of a limited-solubility 50% copper — 50% lead product.

Equal volumes of lead filings and hydrogen-reduced copper, particle size less than 45 microns, were milled in the shaker mill of the preceding example at a ball-to-powder ratio of 4:1. After 10 minutes the product particles had a hardness of 34.6 Vickers and a particle size of 100-200 microns and, after 30 minutes, 69.5 Vickers and 100-150 microns. In each case the individual composite particles contained the two elements substantially uniformly inter-dispersed, the particle spacing being about 5 microns after 10 minutes and about 1 micron after 30 minutes. The structure did not exhibit striations. This is believed to be due to the fact that lead, which has a melting point of about 600°K, is self-annealing when worked at ambient temperatures.

Because of the large amount of lead present, the composite powder can be cold deformed, e.g., by cold extrusion or cold pressing in a die, into any desired shape, for example, an anti-friction bearing element.

By a similar technique, highly uniform wrought products of the components 50% Ag-50% W for electrical contact materials; 25%-50% Cu/75%-50% W; 80% Au-20% Pb; 50%-95% Pt/50-5% Ag; and 50-95% Pb/50-5% Au may be obtained. In a like manner, compositions within the liquid immiscibility range of 6-63% Cu in the Cu-Cr system, e.g., Cu 70%-Cr 30%; within the immiscibility range of the Cu-Mo system, e.g., from 2-98% Cu, balance Mo can be produced, Silver-nickel compositions suitable for electric contact applications, including Ag 60%-Ni 40%, may be produced, as may beryllium-molybdenum compositions including Be 50%-Mo 50%. Beryllium powder may have a thin oxide coating because of its propensity to surface oxidation. This oxide may be used to provide dispersion-strengthening in the final product.

#### Dispersion-Strengthened Stainless Steel

Stainless steel alloys are particularly prone to segregation when cast into ingots, making the ingots difficult to forge. Thus, the rather slow solidification of large ingots leads to the formation of large dendrites, large, non-uniformly distributed grains, and composition segregates along the length and across the width of the ingots. Prolonged soaking at high temperatures in an attempt to homogenize the metallurgical structure of the ingot generally effects little improvement, and may even cause further grain coarsening, with further adverse effects on hot forgeability, extrusion, or rolling. This tendency to segregation also leads to non-uniform precipitation-hardening response in steels containing hardening constituents. The production of stainless steel by conventional techniques of power metallurgy suffers from the disadvantages already discussed in general above, particularly that of oxidation of the more reactive alloying elements, e.g., chromium, and such precipitation hardeners as aluminium and titanium during processing, and, in the case of dispersion-hardened compositions, the formation of stringers.

One advantageous class of products of the present invention is that comprising wrought dispersion strengthened stainless steels characterized by a high degree of uniformity of composition and, in the case of precipitation-hardening compositions, hardening response, together with freedom from segregation and stringers. This is readily achieved by the use of composite particles of the corresponding composition produced by high energy impact milling to saturation hardness and beyond as described hereinbefore, according to U.S. application No. 790,700, since these composite particles are both statistically and internally substantially uniform.

Stainless steels which can be produced in accordance with the invention may have compositions ranging, by weight, from 4% to 30% chromium, from 0 to 35% nickel, up to 10% manganese, and up to 1.0% carbon, together with from 0.5% to 25%, e.g., 0.05% to 10%, by volume of a dispersoid of a refractory compound, the balance, apart from impurities and incidental ingredients, being iron in an amount of at least 45%. It will be understood that here, as elsewhere in the specification, the percentages of the constituents other than the dispersoid, refer to the composition of the alloy matrix.

More preferably, the steels contain from 8% to 30% chromium, up to 20% nickel, up to 5% manganese and up to 0.25% and more preferably, up to 0.15% carbon together with from 0.05% to 10% by volume of a dispersoid of a refractory compound and the iron content is at least 55%.

As will be appreciated, the stainless steel compositions may contain other alloying additions, e.g., up to 5% silicon, up to 5% molybdenum, up to 8% tungsten, up to 2% aluminium, up to 2% titanium, up to 2% niobium/tantalum, up to 7% copper.

Precipitation-hardenable stainless steels include those containing at least 0.2% by weight of one or more of aluminium up to 2%, titanium up to 2%, niobium up to 2% and copper up to 7%. These steels may also contain up to 0.4% phosphorous and up to 0.3% nitrogen. Preferred amounts of dispersoid range from about 0.05 to 5 volume per cent at sizes below one micron.

Impurities and incidental ingredients that may be present include some sulphur and/or selenium for free machining, etc.

Examples of the types of stainless steel that can be produced in accordance with the invention are given in the XI. Table XI.

To produce the wrought, dispersion-strengthened stainless steel product, a batch of the wrought, composite, mechanically alloyed, dense metal particles of the appropriate composition and preferably having an average size such that the surface area per unit volume of particles is not more than 6,000 cm<sup>2</sup>/cm<sup>3</sup> of particles, i.e., substantially free from particles smaller than 5 microns is hot-consolidated to a wrought metal shape. This may conveniently be effected by hot extrusion of the powder sealed in a metal can, e.g., of mild steel.

Annealing of the heavily cold-worked powder takes place during heating in the can to the extrusion temperature.

Two examples of the production of stainless steels will now be given:

#### EXAMPLE XXII

A mixture comprising, by weight, 27.2% of powdered low-carbon ferrochrome, particle size 44-74 microns, containing Cr 70%, Si 1.01%, SiO<sub>2</sub> 1.35%, Cr<sub>2</sub>O<sub>3</sub> 0.54%, Fe balance; 62.8% of high purity sponge iron powder, particle size less than 150 microns; and 10% of carbonyl nickel powder, average particle size 3-5 microns, was milled in a stirred attritor mill of the type

TABLE XI

AISI Type	% C	% Mn	Nominal Composition			% Ni	Others
			% Si	% Cr			
I Austenitic Steels							
201	0.15 max	5.50-7.50	1.0 max	16-18	3.5-5.5	0.25N max	
202	0.15 max	7.5 - 10	1.0 max	17-19	4-6	0.25N max	
301	0.15 max	2.0 max	1.0 max	16-18	6 - 8	—	
302	0.15 max	2.0 max	1.0 max	17-19	8 - 10	—	
303	0.15 max	2.0 max	1.0 max	17-19	8 - 10	0.15 min S	
308	0.08 max	2.0 max	1.0 max	19-21	10 - 12	—	
309	0.20 max	2.0 max	1.0 max	22-24	12 - 15	—	
314	0.25 max	2.0 max	2.0-3.0	23-26	19 - 22	—	
316	0.08 max	2.0 max	1.0 max	16-18	10 - 14	2.0-3.0 Mo	
321	0.08 max	2.0 max	1.0 max	17-19	9 - 12	5xC min Ti	
347	0.08 max	2.0 max	1.0 max	17-19	9 - 13	10xC min Nb/Ta	

#### MARTENSITIC STEEL

403	0.15 max	1.0 max	0.5 max	11.5-13	—	—	
414	0.15 max	1.0 max	1.0 max	11.5-13.5	1.25-2.5	—	
431	0.20 max	1.0 max	1.0 max	15-17	1.25-2.5	—	
440B	0.75-0.95	1.0 max	1.0 max	16-18	—	0.75 Mo max	
440C	0.95-1.2	1.0 max	1.0 max	16-18	—	0.75 Mo max	
501	0.1 max	1.0 max	1.0 max	4-6	—	0.04-0.65 Mo	

#### Nominal Composition

405	0.08 max	1.0 max	1.0 max	11.5-14.5	—	0.1-0.3 Al	
430	0.12 max	1.0 max	1.0 max	14-18	—	—	
430F	0.12 max	1.25 max	1.0 max	14-18	—	0.15 S min	
446	0.2 max	1.5 max	1.0 max	23-27	—	0.25 N max	

#### Nonstandard Grades

AISI Type	% C	% Mn	% Si	% Cr	% Ni	Others
316 F	0.6	1.5	0.5	18	13	2.25 Mo 0.13P, 0.15S
418	1.17	0.4	0.3	12.75	2.0	3.0 W
Stain- less W	0.07	0.5	0.5	16.75	6.75	0.8 Ti 0.2 Al
17-4 PH	0.04	0.4	0.5	16.50	4.25	0.25 Nb 3.6 Cu
17-7PH	0.07	0.7	0.4	17.0	7.0	1.15 Al
PH 15-7	0.07	0.7	0.4	15.0	7.0	1.15 Al
Mo						2.25 Mo
17-10P	1.12	0.75	0.5	17.0	10.5	0.28 P

shown in FIG. 1 operated at 176 r.p.m. at a ball-to-powder ratio of 24:1 in two batches, the first for 16 hours and the second for 48 hours. Each product consisted of composite particles of average size 125–135 microns, the particles milled for 48 hours having a much finer and more homogeneous microstructure. The hardness of the powder as-produced and after various heat-treatments is shown in Table V, which shows that the hardness of the 48-hour powder was retained to a greater extent on heating.

TABLE XII

Heat-treatment	Milled 16 hours	Milled 48 hours
	Hardness (Vickers)	
As milled	785	794
30 mins./982°C.	381	523
30 mins./1066°C.	324	409
1 hour/1204°C.	—	200–220

After heating for 30 minutes at 1,066°C. the internal structure of the 48-hour particles was homogeneous, and compacting at 56.2 kg/mm<sup>2</sup> gave a compact having density of 74% of the true density and a green strength of 76.2 kg/cm<sup>2</sup>. The initial hardness of the particles was remarkably high compared with the hardness of 233 Vickers of a commercial atomised stainless steel powder.

## EXAMPLE XXIII

Another stainless steel composition was produced by dry milling a mix containing 84 g. of carbonyl nickel powder of an average particle size 3–5 microns, 341 g. of high purity ferrochrome powder (0.1% SiO<sub>2</sub>, 70% Cr, balance Fe), average particle size 120 microns and 763 g. of high purity sponge iron powder (0.032% carbon, 0.115% silica) of particle size less than 150 microns for 40 hours in air in an attritor mill, run at 176 r.p.m. with a ball-to-powder ratio of 18:1 by volume. The resulting composite particles had an average particle size of 85 microns. Extrusion of the product, vacuum-sealed in a mild steel can, to rod at an extrusion ratio of 12.5:1 at 1,038°C., gave a product analysing Ni 9%, soluble Cr 20%, Si 0.09%, Cr<sub>2</sub>O<sub>3</sub> 2.15%, Fe balance, which contained a finely divided grayish dispersoid uniformly distributed therein. The dispersoid is believed to have been chromium oxide. At room temperature, the material exhibited a tensile strength of 137.5 kg/mm<sup>2</sup>, a yield strength (0.2% offset) of 121.0 kg/mm<sup>2</sup>, an elongation of 7.5%, a reduction in area of 29% and a modulus of elasticity of 18.8 × 10<sup>3</sup>kg/mm<sup>2</sup>. The material had a Vickers hardness of 421 and was very slightly ferromagnetic.

After heating for 90 hours at 1,093°C. it was non-magnetic and had a Vickers hardness of 390, and at 650°C. it had a stress-rupture life of 44.9 hours with 2.5% elongation under a stress of 24.6 kg/mm<sup>2</sup>. At 816°C. and 7 kg/mm<sup>2</sup> load sample was unbroken after 70 hours.

The properties clearly demonstrated this material was dispersion-strengthened.

## EXAMPLE XXIV

In producing a dispersion-strengthened, precipitation hardenable, wrought stainless steel product of the 17–7 PH type containing, by weight, 0.07% C, 0.7% Mn,

0.4% Si, 17% Cr, 7% Ni, 1.15% Al, and 2.5% zirconia, the balance, apart from impurities, being Fe, the following starting materials are employed: (a) low carbon ferrochrome containing about 70% chromium and some silicon of particle size 44–75 microns; (b) high purity sponge iron of particle size less than 150 microns; (c) carbonyl nickel powder of about 3 to 5 microns average size; (d) ferroaluminium containing about 65% aluminium and zirconia of about 400 Angstroms average size. A 900 gram batch proportioned to yield the foregoing composition is placed in the attritor mill as described hereinbefore and dry impact milled in a nitrogen atmosphere for 48 hours at 176 r.p.m. using a 3.8 litre volume of nickel pellets in size at a ball-to-powder ratio of 24:1. After the 48-hour milling the composite particles were of optimum uniformity, and were of about 100 microns average particle size.

After removal from the mill, and passing through a 177 micron screen, the powder was vacuum sealed by welding in a mild steel can. The canned powder was then heated for 1.5 hours to 1,038°C., and extruded to rod at an extrusion ratio of 16:1, the extruded material having approximately the nominal composition of 17–7 PH stainless, except for the presence of a highly uniform dispersion of finely divided zirconia (about 400 Angstroms in average size). The extruded rod is solution annealed at 1,200°C., reheated at about 760°C. for 1½ hours, air cooled and again reheated at 565°C. for 1½ hours and cooled. Thus, the steel is strengthened using the two-fold effect of dispersion-strengthening and precipitation hardening.

A special group of two-phase stainless steels is now known which are compositionally adjusted to provide a micro-structure containing ferrite and either martensite or austenite. These steels contain 2%, preferably 4.5% to 8% or 12% nickel, 18%, preferably 23% to 28% or even 35%, chromium, up to 1.5% titanium, up to 1% vanadium, balance essentially iron. It is found that powder mixtures of powders proportioned to yield such steels milled to saturation hardness and beyond in a high energy impact mill, e.g., an attritor, exhibit exceptionally fine two-phase structures when hot consolidated by extrusion or hot forging of the canned powders at temperatures in the range of e.g., 1,700°F. to 2,000°F. Such fine-structured or microduplex structural consolidated materials exhibit superplasticity at elevated temperatures.

## High Carbon Tool Steels

High carbon tool steels are particularly prone to segregation during solidification of the ingot when made by melting methods, with the formation of large dendrites and of segregates or aggregates of carbide. The carbides are brittle and adversely affect the ductility of the ingot, but the segregates or aggregates may, with difficulty, be dispersed to a limited extent by mechanical working of the ingot. Even so, the carbide tends to be distributed in the forged or hot-worked product as elongated stringers in the direction of working, with areas between them impoverished in carbides.

It is also difficult to obtain good composition homogeneity by solid state diffusion at elevated temperatures when powder metallurgy methods are used, since such alloying ingredients as chromium, tungsten, and molybdenum diffuse only sluggishly in the powder condition.

The use of a composite powder produced by dry high energy milling of starting powder mixtures propor-

tioned to provide a high carbon tool steel composition as the starting material for the powder metallurgical production of high speed tool steels enables the production of wrought high carbon tool steel characterized by a substantially uniform dispersion of finely divided carbides; and substantial freedom from carbide segregates and aggregates. The degree of uniformity of the structure depends on the uniformity, both statistical and internal, of the composite particles. The increased rate of diffusion and alloying resulting from the high degree of cold work in the composite particles is particularly advantageous in overcoming the sluggish diffusion tendencies of the alloying elements.

Broadly speaking, the tool steels of the invention contain from 0.7% to 4%, e.g., 0.9 to 3.5%, carbon, and at least 0.1%, advantageously at least 1%, of at least one of the alloying elements chromium, vanadium, tung-

sten and molybdenum, up to 2% silicon, up to 2% manganese, up to 5% nickel and up to 15% cobalt, the balance (at least 40%), apart from impurities being iron.

The alloying elements may advantageously be present in the ranges 3% to 15% chromium, up to 10% or 20% vanadium, up to 25% tungsten and up to 12% molybdenum. A particularly useful CR-V-W tool steel composition is one containing Cr 3 to 9%, V 0.3 to 10%, W 1 to 25%, Mo 0 to 10%, Fe balance. A particular advantage of the invention is that carbide formers such as tantalum, niobium, hafnium, zirconium and titanium can be added in amounts up to 15% and well distributed in the form of carbides in the resulting tool steel composition. Examples of specific alloys that may be made are given in the following table XIII, the balance of each composition being iron.

TABLE XIII

Type Steel	Nominal Composition % by Weight								
	C	Mn	Si	Cr	Ni	V	W	Mo	Co
Chromium 0.85-1.0		0.6-0.8	0.1-0.4	0.15-0.3	—	—	—	—	—
Chromium- Molybdenum 0.9-1.25		0.3-0.7	0.1-0.4	1.1-1.5	—	—	—	0.3-0.5	—
Tungsten- Finish- ing Steel	1.25-1.40	0.1-0.4	0.1-0.5	0.2-0.4	—	—	3.25-4.0	0.2-0.4	—
Semi- high Speed Steels	1.15-1.25 1.35-1.45 1.05-1.15	0.1-0.4	0.1-0.4	3.75-4.25	—	3-3.3	—	4.0-4.5	—
Air-Hardening Die Steels	0.9-1.05	0.4-0.85	0.1-0.4	4.75-5.25	—	0.15-0.5	—	0.9-1.15	—
High Car- bon, High Chro- mium Die Steels	1.4-1.6 2.1-2.3 2.0-2.2	0.2-0.4	0.1-0.4	11.5-12.5	—	0.2-1.0	—	0.7-0.9	—
Wear Resis- tant Die Steels	2.15-2.5 2.1-2.3	0.3-0.8 0.3-0.5	0.3-0.8 0.1-0.4	5-5.5 3.75-4.25	—	3.75-5.0 3.75-5.0	0.95-1.3	0.8-1.3	—
Chro- mium Nickel	0.9-1.1	0.03-0.5	0.1-0.4	0.5-0.8	1.2-1.6	—	—	—	—
Tung- sten Types	0.8-0.85 0.95-0.98 0.97-1.03	0.1-0.4	0.1-0.4	4-4.25	—	2-2.15	18-18.5	0.5-0.75	—
Tungsten-Cobalt Types	0.7-0.75 1.5-1.6 0.75-0.85	0.1-0.4	0.1-0.4	4-4.5 4.5-4.75 4.0-4.5	—	1.0-1.25 4.75-5.0 1.6—	18-19 12.5-13.5 18.75-20.5	0.6-0.8 0.4-0.6 0.6-0.8	4.75-5.25 4.75-5.25 11.5-12.25
Molybdenum Types	0.78-0.85 0.97-1.03	0.1-0.4	0.1-0.4	3.75-4.0	—	1-1.25 1.9-2.1	1.5-1.65 1.5-1.75	8-9 8.5-8.75	—
Molybdenum- Cobalt Types	0.8-0.85 0.87-0.93	0.1-0.4	0.1-0.4	3.75-4.25	—	1.1-1.4 1.85-2.25	1.5-1.8 1.3-1.6	8.25-8.5 8.45-8.95	4.75-5.25 8-8.5

TABLE XIII - Continued

Type Steel	C	Mn	Si	Nominal Composition % by Weight			W	Mo	Co
				Cr	Ni	V			
Tungsten-Molybdenum Types	1.0-1.1	0.1-0.4	0.1-0.4	4-4.25	—	2.4-2.55	6-6.25	5.7-6.25	—
	1.25-1.3	0.1-0.4	0.1-0.4	4.25-4.5	—	3.75-4.25	5.5-6.0	4.5-4.75	—
Tungsten-Molybdenum-Cobalt Types	1.5-	1.6	0.1-0.4	0.1-0.4	4.0-4.75	—	4.75-5.25	6.25-6.75	3.0-5.0
Self-Hardening Type	2.25	1.5	0.25	2.0	—	—	11.0	—	—
Special Wear-Resistant Ore Steel	3.25	0.3	0.3	1.0	—	12.0	—	1.0	—

Besides the dispersion strengthening of the tool steels that results from the presence of the extremely finely dispersed carbides, other dispersoids may be incorporated in the composite powder used to form the steels, and thereby in the steels themselves, in an amount of 0.05 to 25%, preferably not more than 10%.

In making the steels, composite powder of the desired composition may be hot consolidated to a wrought metal shape, e.g., by vacuum packing a charge of the particles into a mild steel can which is then heated to 425°C. under vacuum, quenched under vacuum, welded shut, followed by hot extrusion, usually at a temperature of about 815°C., or more, e.g., 1,038°C. to 1,260°C. Homogenisation and annealing can be accomplished during the heating of canned powders prior to extrusion.

Some examples of the production of wrought tool steels by the invention are as follows:

#### EXAMPLE XXV

In producing a complex high-carbon tool steel containing 20% tungsten, 12% cobalt, 4% chromium, 2% vanadium, 0.8% carbon, balance iron, a blend is made of 28.6 g. of 70% V-30% Fe master alloy of particle size less than 150 microns; 57.2 g. of a 70% Cr-30% Fe master alloy of particle size less than 150 microns; 200 g. of 10 micron W powder; 120 g. of cobalt powder of particle size less than 44 microns; 8.0 g. of graphite flakes of particle size less than 150 microns; and 586.2 g. of 65 micron sponge Fe powder. This mixture is dry impact milled in an attritor mill of the type shown in FIG. 1, for 40-50 hours at 180 r.p.m. using 6.2 mm. hardened steel balls at a ball:powder ratio of 20:1. The composite powder thus produced had a microstructure comprising a substantially homogeneous interdispersion of all the constituents. After vacuum-sealing in a mild steel can, the powder was extruded at 1,175°C. at a ratio of 16:1 to a wrought bar free from carbide dendrites, segregates and aggregates.

The complex high speed steel product is hardened by heating to a temperature of 1290°C. for 5-10 mins. followed by oil quenching to room temperature, the cooled steel being thereafter subjected to double tempering by heating to a temperature of 565°C. for about 2 hours, air-cooling and re-heating to 565°C. for an additional 2-hour period.

#### EXAMPLE XXVI

A wrought high carbon steel containing 0.85% C, 0.2% Cr, 0.7% Mn, 0.3% Si, balance iron, was produced as follows. A brittle high carbon master alloy containing 4.25% C, 1% Cr, 3.5% Mn, 1.5% Si, balance iron, was chill-cast and crushed to particles smaller than 75 microns. The resulting powder (400 g.) was mixed and uniformly blended with 1600 g. of 65 micron high purity sponge iron powder, and the mixture was dry impact milled as in Example XXV using 6.2 mm hardened steel balls at a ball-to-powder ratio of 18:1 and an agitator speed of 175 r.p.m. for 45 hours to obtain a highly cold-worked composite metal powder having a substantially homogenous interdispersion of all of the alloying constituents. The composite powder was vacuum packed in a mild steel can which was welded shut, heated to 1095°C. and then hot-extruded to a round rod at an extrusion ratio of 16:1. This steel, which was free from carbide segregates and aggregates, was hardened by oil quenching from an austenitizing temperature of 788°C., followed by tempering at a temperature of 177°C.

#### EXAMPLE XXVII

To make a wrought semi-high speed steel composition having the composition: 1.2% C, 4% Cr, 3% V, 4% Mo, 0.3% Mn, 0.3% Si, balance iron, a brittle high-carbon master alloy containing 4.8% C, 16% Cr, 12% V, 12% Mo, 1.2% Mn, 1.2% Si, balance iron, was chill cast and then crushed to particles smaller than 75 microns. 400 g. of this powder were mixed with 1200 g. of high purity 65 micron sponge iron powder and the mixture was dry impact milled as in Example XXV for 48 hours at 175 r.p.m. using 6.3 mm. hardened steel balls at a ball-to-powder ratio of 18:1 by volume. The highly cold-worked composite metal powder thus obtained had a microstructure comprising a substantially homogeneous interdispersion of all of the alloying constituents and was used to make wrought tool steel shapes by hot extrusion at 1,095°C. in a mild steel can which was evacuated and welded shut. Square rod was produced at an extrusion ratio of 15:1. A tool made from the rod may be heat treated by quenching from 1,232°C. in oil and then tempering (secondary hardening) by heating to 538°C. and holding for 1 hour with good response.

## EXAMPLE XXVIII

In producing a wrought high-C high-speed steel containing 2.5% C, 4.0% Cr, 2.5% Mo, 5.0% Co, 7.0% V, 6.0% W, balance Fe, a blend was first made of 112.5 g. of graphite flakes, 432 g. of a 70% V — 30% Fe master alloy powder, 180 g. of Cr powder, all smaller than 150 microns, 113 g. of Mo powder and 225 g. of Co powder bulk smaller than 45 microns, 270 g. of 10 microns W powder and 3191 g. of 65 micron sponge iron powder. This blend was dry impact milled for 15 hours in a horizontal stirred ball mill containing 91 kg. of hardened steel balls at an impeller speed of 245 r.p.m. in a nitrogen atmosphere, to give a highly cold-worked composite metal powder having a microstructure comprising a substantially homogeneous interdispersion of all the alloying elements.

The powder was vacuum packed in a mild steel can which was welded shut and extruded to rod at 1,093°C. at an extrusion ratio of 16:1. The extruded bar had the remarkably high hardness of 62.5 Rc. A tool was made from this bar was hardened by heating slowly to 870°C, then heated to 1205°C, held for 5 minutes and oil-quenched. After double-tempering by heating twice for 2 hours at 538°C. and air-cooling, the hardness was as high as 67 Rc.

The structure of this complex high carbon steel was exceptionally fine and uniform containing less than about 5 percent by volume of segregated regions exceeding 10 microns in size. The microstructure of this very high carbon tool steel was strikingly finer and much less segregated than that of conventional tool steels at much lower carbon and other alloy contents.

In producing products containing dispersed oxides, the composite particles employed in the process need not contain the oxide finally desired. Instead, composite particles may be used containing constituents that react when subsequently heated to form refractory oxides or other refractory phases not initially present. Thus, composite particles may be made having intimately distributed therethrough metals that form stable refractory oxides, for example, yttrium, lanthanum, cerium, thorium, chromium, silicon, aluminum, beryllium or rare earth metal mixtures such as didymium, together with a less stable oxide of another metal, e.g., nickel oxide, and other alloying constituents. Alternatively the oxygen may be added as adsorbed oxygen or gaseous oxygen in the milling atmosphere which becomes adsorbed and mechanically alloyed with the solid constituents of the powder mix. Such powders can then be consolidated and heated to permit oxidation of the metal having the stable oxide by diffusion of oxygen from the less stable oxide or metastable mechanically alloyed oxygen. By controlling the effective interdiffusion distance over which the oxygen would be required to travel to less than 1 micron and even to less than 0.5 micron, the refractory oxide particles can be produced in a very fine state of dispersion by heating for only a short time. The process may advantageously be used to make nickel or nickel-containing alloys dispersion strengthened with lanthana, yttria, thoria, etc., from composite particles containing the corresponding metal and mechanically alloyed oxygen. If more than one oxidisable metal is present, the process may be controlled by limiting the oxygen supply to the amount necessary to oxidize only the metal with the most stable oxide.

The following example illustrates the use of this procedure to make a nickel alloy dispersion strengthened with alumina.

## EXAMPLE XXIX

A mixture of 781 g. of carbonyl nickel powder of particle size 3–5 microns; 44 g. of nickel oxide (NiO) particle size less than 44 microns; and 75 g. of an 80% Ni — 20% Al master alloy powder, particle size less than 44 microns is dry milled in a nitrogen atmosphere for 48 hours in the mill of Example I at a ball-to-powder ratio of 22:1 and 176 r.p.m. The composite particles formed, after removal of a small coarse fraction, are vacuum sealed, in a mild steel can. The sealed can is then heated at 982°C. for 2 hours to allow the constituents in the composite metal particles to diffuse into each other and to allow the oxygen of the nickel oxide to react with the aluminum and convert a stoichiometric portion of it to  $Al_2O_3$ , which is formed as a fine dispersion throughout the alloy. The heated can is then extruded with an extrusion ratio of 16:1.

Two compatible constituents may also be combined in the same alloy by separating them with a third mutually compatible constituent, the two incompatible constituents being introduced in successive milling operations. Bearing in mind that harder or less ductile constituents will tend to become dispersed within softer or more ductile constituents, many combinations of constituents may be utilized in a hierarchy. Such a hierarchical composite may be combined with one or more other hierarchical composite in a common matrix. In this way, novel structures may be produced which cannot be made in any other way.

A hierarchical process of this kind is illustrated in the following example.

## EXAMPLE XXX

A charge consisting of 50% by volume of 5 microns tungsten powder and 50% by volume of zirconium oxide powder having a particle size of 0.03 micron was dry milled in a high speed laboratory shaker mill for about three hours. A composite powder comprising zirconia distributed through a tungsten matrix was produced. Forty volume percent of this powder was then mixed with 60% of carbonyl nickel powder having an average particle size of 3 to 5 microns and the mixture was again dry milled in the high speed shaker mill for a total of 2 hours. Hard tungsten-zirconia powder particles were comminuted and distributed in the product powder as a finely dispersed phase. The resulting relatively coarse product powder contained by volume 20% zirconium, 20% tungsten and 60% nickel in hierarchical relation with minimal contact between zirconia and nickel.

It is to be understood that in the foregoing examples wherein a dispersion-strengthened product, e.g., a dispersion-strengthened superalloy or stainless steel, was produced, the product contained less than 10%, by volume, of segregated regions exceeding 3 microns in size and more usually such regions did not exceed 1 micron or even 0.5 micron in size.

Other wrought metal systems that are advantageously produced by the invention include the following:

1. compositions that are difficult to make because of the low boiling point of one of the constituents, e.g., alloys including lithium such as Ni-1% Li, for purposes requiring corrosion resistance; systems

including boron such as nickel-boron compositions and boron-containing steels such as 18-8 Cr-Ni or AISI Type 347 steels with boron.

- 2. compositions in which one component is highly reactive e.g., rare earth metal compositions such as RCo<sub>5</sub> for permanent magnets, where R is a rare earth metal such as cerium or samarium. The rare earth metals react readily with the refractory linings of crucibles used for melting, so that levitation melting or consumable arc melting into a cooled metal mould is normally employed, leading to an undesirably large grain size.
- 3. Iron-silicon alloys for transformer laminations, e.g., Fe/5-7% Si with or without up to 10% Ni to improve magnetic properties.

The invention is particularly applicable to those deformable metals having an absolute melting point of over 600°K. and, more preferably, over 1,000°K., as such metals are capable of being heavily worked with the milling process. With regard to lower melting metals, which tend to be self-annealing under heavy working conditions at substantially ambient temperature, these can be processed with other metals at ambient temperatures to produce useful wrought composite metal powder. On the other hand, where the need calls for it, such metals can be processed at below their recrystallization temperature by working at substantially below ambient temperatures to thereby achieve a substantially steady state balance between the welding and grinding factors.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

I claim:

- 1. A mechanically alloyed composite metal powder, the particles of which are of substantially saturation hardness, have a plurality of constituents and have an

alloy composition from the group consisting of platinum with up to about 50% palladium, platinum with about 3.5 percent to about 40 percent rhodium, platinum with up to about 35% iridium, platinum with up to about 8% tungsten, gold alloys containing about 7% to about 30% platinum, about 1% to 13% palladium, about 7% to about 16% silver, about 7% to about 14% copper, up to about 1% nickel, up to about 2% zinc and the balance essentially gold, lead-copper alloys, copper-tungsten alloys, silver-tungsten alloys, copper-chromium alloys, silver-chromium alloys, copper-molybdenum alloys, silver-molybdenum alloys, silver-manganese alloys, silver-nickel alloys, beryllium-molybdenum alloys, silver-platinum alloys, platinum-gold alloys and zinc-base alloys containing up to about 0.35% lead, up to about 30% cadmium, up to about 1.5% copper, up to about 1.5% titanium, up to about 0.1% magnesium and up to 4.5% aluminum, said particles containing up to about 25%, by volume, of a fine refractory dispersoid having an average size of less than 1 micron and said particles being characterized metallographically by an internal structure comprising said constituents in fragmented form intimately united together and interdispersed, with the minimum dimension of said fragments not exceeding about 10 microns.

- 2. A mechanically alloyed metal powder according to claim 1 having an alloy composition comprising metal constituents of limited solubility from the group consisting of copper with about 1% to about 95% lead, iron with about 1% to about 95% copper, tungsten with about 2% to about 98% silver, tungsten with about 25% to about 50% copper, copper with about 5% to about 95% chromium, copper with about 2% to about 98% molybdenum, nickel with about 60% silver and molybdenum with about 50% beryllium.

- 3. A mechanically alloyed metal powder according to claim 1 wherein said dispersoid is a refractory oxide in the amount of about 0.05% to about 10% by volume and wherein the minimum dimension of said fragments does not exceed about 3 microns.

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