

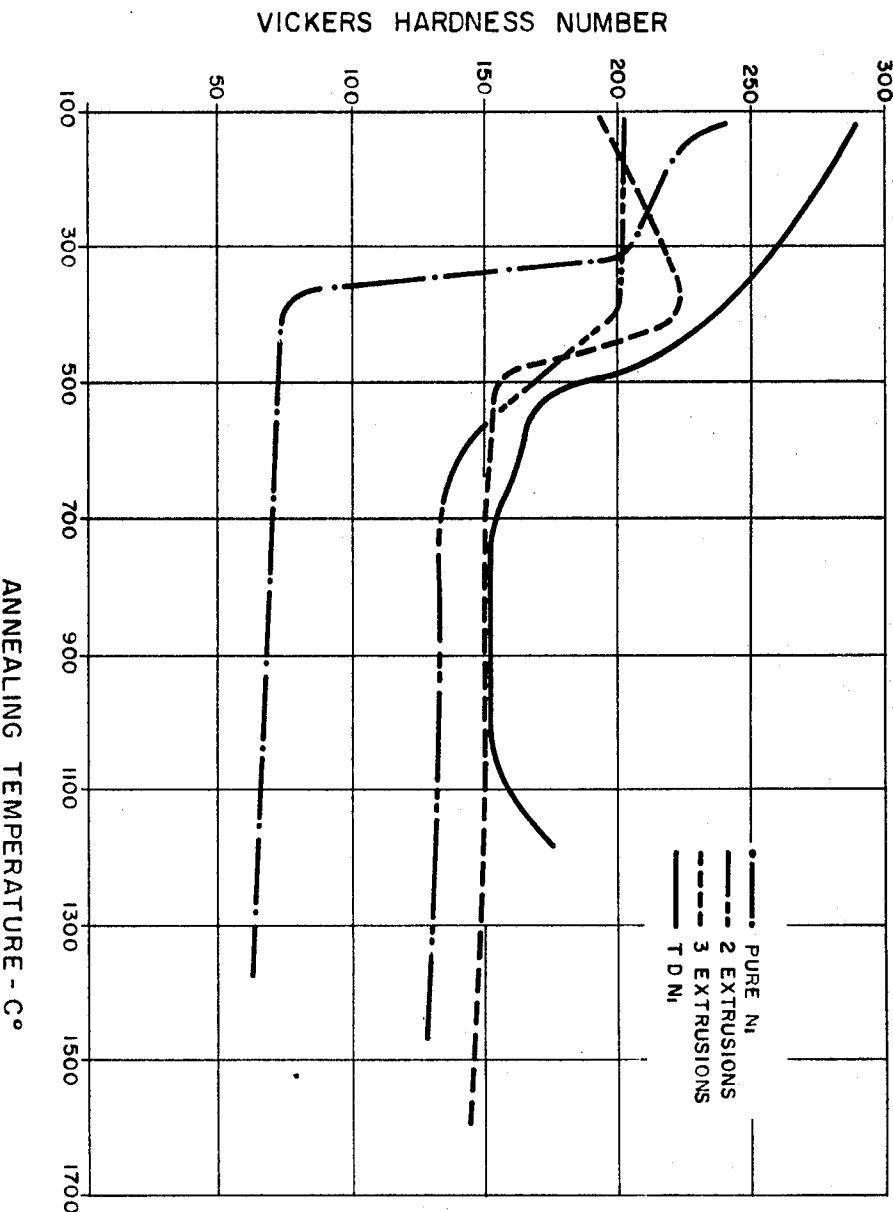
April 22, 1969

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3,440,042

METHOD OF PRODUCING DISPERSION HARDENED METALS

Filed Jan. 28, 1965



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3,440,042

METHOD OF PRODUCING DISPERSION HARDENED METALS

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Filed Jan. 28, 1965, Ser. No. 428,705

Int. Cl. C22c 1/10, 1/05

U.S. Cl. 75—206

13 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a method of producing dispersion hardened metals by mechanically blending particles of a matrix metal and dispersoid particles, and then extruding and re-extruding the blend until the original particles of matrix metal have been transformed into elongated fiber having an average diameter of less than one micron.

This invention relates to dispersion hardened metals, and more particularly to an improved method of dispersing minute particles of metal oxides in selected metals and alloys.

Metallurgists are constantly striving to obtain new additives, reactants, alloys and processing procedures which will give them a metal product having increased or altered, chemical or physical, property characteristics. Despite the development of so-called "super alloys" which have been developed for service at extremely high temperatures, high stress and strain, and maximum possible service life; metallurgists still seek methods of further improving even these "super alloys."

One known method of producing improved physical property characteristics, such as improved strength at elevated temperatures, improved stress rupture characteristics, improved creep strength characteristics, and improved service life at high stress; is to disperse minute particles of metal oxide in the matrix metal or alloy, producing what is commonly called a dispersion hardened metal or alloy. The dispersed particles of metal oxide are frequently referred to as "dispersoid particles."

As used herein, the words "dispersoid" and "dispersoid particles" shall be understood to denote metal oxide particles, and the term "metal" shall be understood in the broad sense so as to include alloys, rather than in the limited sense where it would include only pure metallic chemical elements.

Substantially improved properties of the type noted above have been obtained when the dispersoid particles are less than one half a micron in size, and the distance between any two dispersoid particles is less than one micron. Some lesser improvement can be found, however, even when somewhat larger particles of oxide are dispersed, and/or when the distance between dispersoid particles is more than one micron.

Previous attempts have been made to produce dispersion hardened metals by purely mechanical, or quasi-mechanical steps, e.g. mechanically stirring together metal and metal oxides particles of the aforementioned size, and compressing the mixed powders into a solid mass. These prior methods did not yield a product possessing optimum physical property characteristics of the type previously noted.

These various prior methods involve several common problems, particularly: the tendency of oxide particles

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smaller than one half micron to agglomerate and to remain agglomerated, and the rapid oxidation of metallic particles smaller than one micron, particularly during the heavy mixing required to obtain good dispersion. It has, therefore, become necessary to employ, additionally, one or more chemical steps to produce dispersion hardened metals having near optimum physical property characteristics. This can be accomplished by adding a chemical reduction procedure to an otherwise mechanical process. The chemical reduction procedure, of course, greatly limits the range of both matrix materials and metal oxides which may be employed, since only readily reducible matrix materials and/or relatively non-reducible metal oxides can be employed.

Another method of producing dispersion hardened metals is to precipitate chemically the oxide of the matrix metal, and the metal oxide to be dispersed, from a single solution. The precipitate is separated, washed, dried, and then subjected to a chemical reduction procedure, e.g. reduction using hydrogen gas. After purification and reduction are complete, the product is solidified, e.g. by extrusion.

The essentially chemical methods of producing particle dispersions, e.g. co-precipitation, are of very limited application since they may only be employed with matrix metals and metal oxide particles having a very limited range of chemical properties, and they preclude the use of most alloys as the matrix metal. They are also indirect, involving the handling of large volumes of liquids, and they require many time-consuming and expensive procedures such as filtering and washing of precipitates.

The previously required chemical treatment steps can now be eliminated. The present invention provides an essentially mechanical method of producing dispersion hardened metals by mixing metal oxide particles of less than one half micron in size with metal particles of twenty to thirty microns or more. The mixture is then extruded and re-extruded during which the large metal particles become elongated until they are essentially elongated fibers of metal with an average diameter of less than one micron. The increased metal particle size of the starting material significantly reduces oxidation of the metal since the total exposed surface area of metal powder is greatly reduced. The agglomerates of dispersoid particles are broken down since the agglomerated mass also tends to become greatly elongated during the extrusions, and subsequent extrusions appear to further aid breakdown of the agglomerates.

One object of this invention is to provide an improved mechanical method of producing dispersion hardened metals and alloys.

Another object of this invention is to produce by a mechanical method dispersion hardened metals and alloys wherein oxidation of the matrix is substantially reduced.

Another object of this invention is to provide an improved mechanical method of producing dispersion hardened metals whereby the necessity of a chemical reduction step can be eliminated.

Further objects, features and advantages will in part be obvious and will in part be seen from the following detailed description, taken in conjunction with the accompanying drawing wherein the figure is a graph depicting hardness at room temperature after heating metals to various elevated temperatures.

The present invention overcomes the problems of oxidation of the matrix metal by providing a method which permits the use of large particles of matrix metal. Our

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experiments have shown that when particles having an average diameter d_1 , are extruded through an extruder having a chamber diameter A, and a die orifice diameter B, the average diameter of the particles after extrusion, d_2 , in a plane perpendicular to the direction of extrusion, can be determined according to the following formula:

$$d_2 = d_1 (B/A)$$

Thus, where particles of nickel metal having a diameter d_1 of 25 microns are extruded through an extruder having a chamber diameter A of 3 inches and a die orifice diameter B of 0.6 inch, the elongated fibers of metal within the extruded rod of nickel metal will have an average diameter d_2 of 5 microns. A second extrusion would reduce the average diameter to 1.0 micron, and a third extrusion would then reduce the average diameter to 0.2 micron as shown in the following equations in which d_2 of the first extrusion becomes d_1 for the second extrusion, and d_2 from the second extrusion becomes d_1 for the third extrusion:

First extrusion: $d_2 = 25(0.6/3) = 5.0$ microns

Second extrusion: $d_2 = 5.0(0.6/3) = 1.0$ micron

Third extrusion: $d_2 = 1.0(0.6/3) = 0.2$ micron

It will, of course, be seen that the formula above can be expanded so that when the rod obtained from the first extrusion is subsequently re-extruded until there have been n extrusions, we can say that:

$$d_2 = d_1 (B/A)^n$$

Using the same original figures as those used above, $d_1 = 25$; $A = 3$; $B = 0.6$; and a total of three extrusions ($n = 3$), this new equation works out:

$$d_2 = 25(0.6/3)^3 = 25(0.2)^3 = 25(.008) = 0.2$$

Thus, by selection of the extruder chamber diameter, the die orifice diameter and the number of extrusions, we can greatly vary the diameter of the starting metal particles. By starting with particles of a relatively large size we have greatly reduced the surface area of metal exposed to oxidation, and yet as the particle size is reduced to the desired range there is no substantial increase in the surface area of metal exposed to oxidation because of the compacting of the particles into a rod.

Inasmuch as all extruders do not have perfectly cylindrical extrusion chambers and/or a perfectly round die orifice, it may be more convenient to mathematically translate the above formulas so as to put them in terms of areas. Thus where the extrusion chamber has a cross-sectional area P, perpendicular to the direction of extrusion, and the die orifice has a cross-sectional area Q, perpendicular to the direction of extrusion a simple mathematical transposition of the above formula will yield a formula as follows:

$$d_2 = d_1 (Q/P)^{1/2}$$

As previously noted, for purposes of this invention the term metal should be understood to include alloys, since alloys may be employed with equal facility as the matrix metal. Any method which requires a chemical reduction step will almost by definition preclude the use of alloys as the matrix metal.

As examples of metals and alloys which may be employed as a matrix metal for purposes of the present disclosure, mention may be made of the following:

Cadmium	Platinum
Cobalt	Rhenium
Copper	Rhodium
Gold	Any of the so-called "super alloys"
Iron	Ruthenium
Lead	Silver
Molybdenum	Tin
Nickel	Tungsten
Osmium	Brass
Palladium	Stainless steel

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As examples of suitable metal oxides for dispersion in a matrix metal according to the present invention mention may be made of the following:

Al ₂ O ₃	SiO ₂
BaO	Ta ₂ O ₅
BeO	ThO ₂
CaO	TiO ₂
CeO ₂	UO ₂
Cr ₂ O ₃	V ₂ O ₃
HfO ₂	Y ₂ O ₃
La ₂ O ₃	ZrO ₂
MgO	ZrSiO ₄
NbO ₂	

Since the novel method of the present invention involves a preliminary mechanical mixing or stirring of the materials to be blended, certain improvements can be made by the use of special mixing equipment such as ultrasonic apparatus, e.g. Branson Sonifier Model S-75 with or without a catenoidal horn.

Improved results can also be obtained by cross-milling the rods obtained from a prior extrusion into small chips. While this crossmilling will tend to break up the long fibers of metal, the average diameter of the fibers after re-extrusion has been found to be substantially the same as the diameter of fibers re-extruded from rods which were not cross-milled. These findings are based on examination of test rods which showed that the average distance perpendicular to the extrusion direction between oxide particles was substantially the same in cross-milled samples and in non cross-milled samples. These observations disclosed that the cross-milling greatly improved the breakdown of agglomerates of oxide to yield more uniform distance between oxide particles parallel to the direction of extrusion.

The following examples are offered by way of illustration and not by way of limitation.

EXAMPLE I

3331.7 grams of nickel powder (Glidden Company nickel powder grade #F-230) and 66.6 grams of Al₂O₃ (Buehler Ltd. #40-6305 A.B. Alpha; 0.3 micron) were mixed in a Hobart mixer for three hours, after which the mixture was placed in a one-gallon jar, a pint jar of Teflon cubes was added to aid mixing, and the gallon jar was placed on a ball mill roller and tumbled for 24 hours at 58 r.p.m.

After removal of the Teflon cubes, the mixture was compacted in a vertical press and outgassed for three days at 1700° F., and then extruded from an extrusion container having a chamber diameter of 3 inches through a die having an orifice diameter of 0.6 inch (1/5 of the chamber diameter). A test rod was selected and photomicrographs of 100× and 600× were made.

The rods obtained from this extrusion were divided into two samples of nearly equivalent size, one to be used below and one to be saved for Example II. The rods from the first sample were then re-extruded in a direction parallel to the original direction of extrusion, using a similar 5 to 1 ratio of chamber diameter to die orifice diameter. A test rod was selected, and photomicrographs of 100× and 600× were made.

The rods obtained in the second extrusion were again re-extruded in a direction parallel to the previous direction of extrusion, using a similar 5 to 1 ratio of chamber diameter to die orifice diameter. A test rod was selected and photomicrographs of 100× and 600× were made.

Comparisons of the photomicrographs taken during the various stages of the example clearly show dispersion and breakdown of the agglomerates of metal oxide to be improved with each subsequent extrusion. Photographs taken using an electron microscope at 10,000× also clearly show dispersion of the dispersoid particles, improved dispersion with the second and third extrusion and improved breakdown of the agglomerates of metal oxide.

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EXAMPLE II

The rods from the second sample from the first extrusion of Example I were then machined into chips by cross-milling, and the chips were compacted and outgassed at 1700° F., then re-extruded using a similar 5 to 1 ratio of chamber diameter to die orifice diameter. One of the re-extruded rods was then checked by photomicrographs of 100× and 600×.

The rods were again machined into chips by cross-milling, and the chips were compacted and outgassed at 1700° F., then re-extruded using a similar 5 to 1 ratio of chamber diameter to die orifice diameter. A test rod was selected and photomicrographs of 100× and 600× were made.

Comparisons of the photomicrographs taken during the various stages of this example clearly show improved dispersion and breakdown of the agglomerates of metal oxide with each subsequent extrusion. Photographs taken using an electron microscope at 10,000× also clearly show dispersion of the dispersoid particles and improved dispersion with the second and third extrusions.

EXAMPLE III

3331.7 grams of nickel powder (Glidden Company nickel powder grade #F-230) and 66.6 grams of Al₂O₃ (Buehler Ltd. #40-6305 A.B. Alpha; 0.3 micron) were mixed in a Hobert mixer for three hours. A 150 gram sample of the mixture was placed in a 400 ml. breaker, and distilled water was slowly added with hand stirring until the mixture was of a thick mud-like consistency. A Branson Sonifier Model S-76 was then set up using a catenoidal Horn with a ½ inch diameter tip, and the horn tip was positioned in the beaker containing the sample mixture with the horn tip ¼ of an inch from the bottom of the beaker. The beaker was then rotated for one hour during which the full output of the ultrasonic generator was employed. The sample mix was dried overnight in an oven at 250° F., compacted in a vertical press and outgassed at 1850° F., then extruded through an extrusion die, similar to that employed in Example I. Photomicrographs of 100× and 600× were then taken of the sample rod.

The rods obtained from this extrusion were divided into two samples of nearly equivalent size, one of which was set aside for Example IV. The rods from the first sample were re-extruded in a direction parallel to original direction of extrusion using a similar 5 to 1 ratio of chamber diameter to die orifice diameter. A test rod was selected, and photomicrographs of 100× and 600× were made.

The rods obtained in the second extrusion were again re-extruded in a direction parallel to the previous direction of extrusion, using a similar 5 to 1 ratio of chamber diameter to die orifice diameter. A test rod was selected and photomicrographs of 100× and 600× were made.

Comparisons of the photomicrographs taken during the various stages of this example clearly show that the use of the ultrasonic apparatus aided dispersion and breakdown of the agglomerates of metal oxide. Photographs taken using an electron microscope at 10,000× also clearly show dispersion of the dispersoid particles improved dispersion with the second and third extrusions, and improved breakdown of agglomerates of metal oxide particles.

EXAMPLE IV

The rods from the second sample, prepared according to Example III were then machined into chips by cross-milling, and the chips were compacted and outgassed at 1700° F., then re-extruded using a similar 5 to 1 ratio of chamber diameter to die orifice diameter. One of the re-extruded rods was then checked by photomicrographs of 100× and 600×.

The rods were again machined into chips by cross-milling, and the chips were compacted and outgassed at

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1700° F., then re-extruded using a similar 5 to 1 ratio of chamber diameter to die orifice diameter. A test rod was selected and photomicrographs of 100× and 600× were made.

Comparisons of the photomicrographs taken during the various stages of this example clearly show that the use of the ultrasonic apparatus aided dispersion and breakdown of the agglomerates of dispersoid particles. Photographs taken using an electron microscope also clearly show dispersion of the particles of metal oxide and improved dispersion with the second and third extrusions.

EXAMPLE V

3331.7 grams of nickel powder (Glidden Company nickel powder grade #F-230) and 66.6 grams of Al₂O₃ (Buehler Ltd. #40-6305 A.B. Alpha; 0.3 micron) were mixed in a Hobert mixer for three hours. An 80 gram sample of the mixture was placed in a 400 ml. breaker, and distilled water was added with hand stirring until the mixture was of a thin fluid consistency. A Branson Sonifier Model S-75 was then set up with a continuous flow chamber, and the fluid sample was stirred and circulated through the chamber. The sample mixture was recirculated through the chamber approximately twenty times during which the full output of the ultrasonic generator was employed. The sample mix was dried overnight in an oven at 25° F. The sample mixture was extruded through an extrusion die similar to that employed in Example I, and photomicrographs of 100× and 600× were made of a sample rod.

The rods obtained from this extrusion were divided into two samples of nearly equivalent size, one of which was put aside for Example VI. The rods from the first sample were then re-extruded in a direction parallel to the original direction of extrusion using a similar 5 to 1 ratio of chamber to die orifice diameter. A sample rod was selected, and photomicrographs of 100× and 600× were made.

The rods obtained in the second extrusion were again re-extruded in a direction parallel to the previous direction of extrusion, using a similar 5 to 1 ratio of chamber diameter to die orifice diameter. A test rod was selected and photomicrographs of 100× and 600× were made.

Comparisons of the photomicrographs taken during the various stages of this example clearly show dispersion and breakdown of the agglomerates of metal oxide. Photographs taken using an electron microscope at 10,000× also clearly show dispersion of the dispersoid particles and improved dispersion with the second and third extrusions.

EXAMPLE VI

The billets from the second sample, prepared according to Example V were then machined into chips by cross-milling, and the chips were compacted and outgassed at 1700° F., then re-extruded using a similar 5 to 1 ratio of chamber diameter to die orifice diameter. One of the re-extruded rods was then checked by photomicrographs of 100× and 600×.

The rods were again machined into chips by cross-milling, and the chips were compacted and outgassed at 1700° F., then re-extruded using a similar 5 to 1 ratio of chamber diameter to die orifice diameter. A test rod was selected and photomicrographs of 100× and 600× were made.

Comparisons of the photomicrographs taken during the various stages of this example clearly show improved dispersion and breakdown of the agglomerates of metal oxide. Photographs taken using an electron microscope at 10,000× also clearly show dispersion of the dispersoid particles and improved dispersion with the second and third extrusions.

After completing the examples, rods were prepared according to Example II and a sample was saved from both the second and third extrusion. These samples were then subjected to annealing treatments at various tem-

peratures and cooled to room temperature after which the Vickers hardness was measured. These test results together with similar data for pure nickel and a chemically produced dispersion hardened nickel have been placed on a single graph, as shown in the figure. The curves and corresponding figures for the chemically produced dispersion hardened metal and the pure nickel are taken from a similar graph prepared by M. C. Inman, K. M. Zwilsky and D. H. Boone and published by the Pratt & Whitney Aircraft Corporation of North Haven, Conn. publication number 63-006, page five. As shown in the figure, the curve for pure nickel is designated Pure Ni; the curve for the chemically produced dispersion hardened metal is designated TDNi, and the two test samples are designated respectively 2 extrusions, and 3 extrusions. In comparing the four curves, it should be noted that slightly better results for the chemically produced dispersion hardened metal and the pure nickel, at temperatures below 400° C., can be attributed to the fact that both of these samples were cold worked before testing. The important portion of the curve is that portion above 500° C. at which temperature each of the curves tends to level out. It will be noted that the curves for the pure nickel sample is considerably lower than any of the other curves, the curve of the sample which was extruded twice is far superior to that of the pure nickel and the curve of the sample extruded three times is substantially the same as that of the chemically produced dispersion hardened metal.

The results graphically depicted in the figure clearly show that the novel method of the present invention produces a dispersion hardened metal having substantially the same properties as dispersion hardened metals produced by the much more expensive chemical method.

This method has the further advantage of providing a means by which many alloys which could not heretofore be dispersion hardened, can now be successfully employed as a matrix metal.

It is apparent that changes and modifications may be made within the spirit and scope of the instant invention; however, it is my intention to be limited only by the appended claims.

As my invention I claim:

1. A method of producing dispersion hardened metals which comprises the steps of mechanically blending particles of a matrix metal and dispersoid particles, extruding the blended particles to produce an elongated solid metallic member and re-extruding said metallic member until said particles of matrix metal are formed into elongated fibers having a diameter of less than one micron.

2. The method according to claim 1 wherein said second metallic member is re-extruded; wherein the particles of matrix metal have an average diameter of less than 25 microns and the dispersoid particles have an average diameter of less than 0.5 micron; and wherein the said extrusions are carried out in an extruder having a chamber diameter to die orifice diameter ratio of 5 to 1.

3. The method according to claim 1 wherein the particles of matrix metal and the dispersoid particles are mechanically blended together in an ultrasonic mixer.

4. The method according to claim 3 wherein water is added to the dispersoid particles and the particles of matrix metal to produce a suspension having a very high viscosity and wherein said suspension is placed in said ultrasonic mixing apparatus.

5. The method according to claim 3 wherein water is added to the dispersoid particles and the particles of matrix metal to produce a suspension having a very low viscosity and wherein said suspension is placed in said ultrasonic mixing apparatus.

6. The method according to claim 1 wherein said first

metallic member is cross-milled into metallic chips before being re-extruded.

7. The method according to claim 2 wherein said first metallic member is cross-milled into metallic chips before being re-extruded and wherein said second metallic member is cross-milled into metallic chips before being re-extruded.

8. The method according to claim 3 wherein said first metallic member is cross-milled into metallic chips before being re-extruded.

9. The method according to claim 1 wherein said metallic member is placed in position to be re-extruded in a direction parallel to the original direction of extrusion.

10. The method according to claim 2 wherein said metallic member is placed in position to be re-extruded in a direction parallel to the original direction of extrusion; and wherein said second metallic member is placed in position to be re-extruded in a direction parallel to the original direction of extrusion.

11. The method according to claim 3 wherein said metallic member is placed in position to be re-extruded in a direction parallel to the original direction of extrusion.

12. A method of producing a dispersion hardened metal which comprises the steps of mechanically blending particles of metal and dispersoid particles; extruding said blended particles through an extruder having an extrusion chamber and a die orifice said extrusion chamber having extrusion chamber diameter and said die orifice having a die orifice diameter to produce an elongated solid metallic member; re-extruding said member until the total number of extrusions is at least equal to n in the formula:

$$1 \text{ micron} = d_1(B/A)^n$$

wherein d_1 equals the average diameter of the original particles of metal, B equals the die orifice diameter and A equals the extrusion chamber diameter; all diameters being expressed in microns.

13. A method of producing a dispersion hardened metal which comprises the steps of mechanically blending particles of metal and dispersoid particles; extruding said blended particles through an extruder having an extrusion chamber and a die orifice said extrusion chamber having a cross-sectional area perpendicular to the direction of extrusion and said die orifice having a cross-sectional area perpendicular to the direction of extrusion to produce an elongated solid metallic member; re-extruding said member until the total number of extrusions is at least equal to n in the formula:

$$1 \text{ micron} = d_1(Q/P)^{n/2}$$

wherein d_1 equals the average diameter of the original particles of metal, Q equals the cross-sectional area of the die orifice and P equals the cross-sectional area of the extrusion chamber; said diameter being expressed in microns, and said cross sectional areas being expressed in the same units of measurement.

References Cited

UNITED STATES PATENTS

2,921,875	1/1960	Schnitzel	75—214 X
3,189,989	6/1965	Ebdon	75—206 X

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U.S. Cl. X.R.

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