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PROCESS FOR MAKING TUNGSTEN AND MOLYBDENUM ALLOYS

Lloyd Ivan Lasdon, Scarsdale, N.Y., assignor to P. R. Mallory & Co. Inc., Indianapolis, Ind., a corporation of Delaware

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3 Claims. (Cl. 75—.5)

This application is filed as a continuation of application Ser. No. 132,306 filed Aug. 8, 1961, and now abandoned.

This process relates to a new method for the production of tungsten and molybdenum co-reduced metal powders for use by the refractory metal fabricating industry in producing parts via standard compacting and sintering techniques.

The process has in its scope, applicability to the combination and/or alloying in any quantitative relationship elements as tungsten and/or molybdenum plus nickel, copper, iron, silver, uranium, etc. or any desired elements that can be reduced to their metallic state from either their soluble salts or from one of their oxides in a hydrogen atmosphere between 700 degrees centigrade and 1100 degrees centigrade.

Currently, there is a great deal of development effort being expended in advanced technological areas on tungsten and molybdenum alloys fabricated by powder metallurgical techniques and in many cases in these alloys difficulties are being encountered that can be attributed to lack of sufficient density, uniformity of physical properties, and inconsistent chemical analysis in different areas of individual pieces, and the inability to provide reproducibility of characteristics in different lots.

Commercially, tungsten alloys are at present being produced by industry in important quantities. Alloys of tungsten, nickel, and copper, known and marketed under individual trade names, but generally referred to as heavy alloys are used as weighting devices, gyrorotors, flywheels, in radiation shielding, etc. They are also being employed on some of our most advanced missile systems.

Tungsten-copper and tungsten-silver combinations are used in important quantities as electrical contact and welding materials.

Tungsten-nickel, tungsten-nickel-iron and tungsten molybdenum, combinations have been under intense investigation for missile and atomic energy applications for some years.

Under existing processes, most of the above described alloys and metal combinations are produced by either intimately, mechanically blending the elements in fine metal powder form in their proper proportions prior to compacting and sintering, or by blending the fine oxides of the desired constituent metallic elements and by co-reducing them in hydrogen atmosphere.

These methods provide, prior to sintering where true alloys are formed, and generally where they are not, mixtures of individual metal particles which may or may not be completely uniform throughout a given finished part. Furthermore based upon the facts that the two or more metal powders will have different densities and almost always considerable differences in their particle size distributions, they tend to segregate on handling, prior to compacting. Individual pieces therefore, whether they form alloys or not, generally have inherent variations in structure.

In some areas where alloys between tungsten and molybdenum and the other constituent elements do not exist, combination commercially by a technique of infiltration is practiced, whereby a skeletal matrix of the re-

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fractory metal is formed, filled with the liquid phase of the other element, then permitted to cool. Here again, lack of uniformity throughout a part occurs because of lack of uniformity of the skeletal matrix, and the natural resistance to penetration of the liquid phase element that some impurities impart. In addition, the same problem exists in some cases as with the previously described two processes, wherein the material is no more than a mixture of crystals of the elements rather than the potentially more homogenous mixture would be at the atomic level.

Generally speaking, my process provides a method for the metallic elements to be combined with tungsten or molybdenum in either of two ways:

(1) Blending at the atomic level, by providing an aqueous solution of all of the metallic elements in soluble compound form, and co-precipitating them prior to co-reduction in hydrogen.

(2) Coating of a precipitated or crystallized tungsten compound with the desired additive elements in aqueous solution with combined blending and drying followed by co-reduction.

(1) In the particular case where it is desired to produce an alloy of tungsten containing 5% nickel and 5% copper.

(a) By the use of our first process; to an ammonium-tungstate solution containing a given calculated amount of tungsten we add the theoretical quantity of copper and nickel in a solution prepared by dissolving their soluble salts (such as their nitrates) in pure aqueous ammonia. Soluble copper and nickel ammonia complexes are formed.

This total mixture is then evaporated with continuous agitation until crystallization is complete. The final dried salt will then contain tungsten, nickel and copper in the 90%-5%-5% proportion.

This combined salt is then co-reduced in a hydrogen atmosphere, and by control of material bed depth, hydrogen flow, and moisture content, temperatures, and furnace residence time, the combined alloy powder is produced to the desired particle size, distribution density, etc.

(b) In producing the same alloy as in Example 1 by the second process described; dry ammonium para-tungstate crystals (produced by standard existing techniques) of 99.9+% purity and fine particle size is weighed and calculated to a given quantity of tungsten. Into a steam jacketed blender a solution of nickel and copper prepared as described in Example 1a containing the desired calculated quantities of each is added in addition to the dry tungsten salt. This mixture is then blended and evaporated slowly to dryness. The finished dry material then consisting of individual tungsten crystals coated with nickel and copper in the proper proportions is then co-reduced as in Example 1.

In a similar fashion as above provided, if it is desired to produce tungsten and/or molybdenum alloys containing other elements then those described soluble salts must first be found that are compatible; that do not volatilize in the high reduction temperatures (but rather decompose); that are economically practical and that are not significantly corrosive to the alloys of furnace construction.

One such example might be a tungsten-iron-nickel alloy powder. The salts used might be either ammonium para tungstate crystals, or ammonium tungstate solution plus either organic iron and nickel salts (formate, citrate, etc.) or iron and nickel nitrate. Proper choice of solvent would be either pure water or dil. or concentrated aqueous ammonia.

Another example would be the production of tungsten-molybdenum alloy powder in any proportion such as 85%W-15Mo, 50W-50Mo. The ammonium solution of

both elements are compatible and can be crystallized or precipitated together as a common salt or one can be crystallized by evaporation onto the other.

Again, silver in the form of its nitrate salt can be dissolved, blended and evaporated onto either tungstic acid, oxide-ammonium tungstate molybdic oxide or ammonium molybdate in desired proportion.

With the processes described above, individual particles of the uncombined elements cannot exist. Homogeneity is assured by the fact that segregation cannot occur since each particle or crystal of metal to be compacted is in itself the desired combination of elements. Evaluation work done on samples of tungsten and molybdenum alloy powders prepared in the above manner over the past two years have shown the following:

- (1) Simplification of fabrication processes for these materials providing (more in the case of the coating process) economic advantages.
- (2) Much greater uniformity of structure providing superior physical properties.
- (3) The greater ability in some cases to reach higher densities with lower sintering temperatures and shorter furnacing times.
- (4) Greater machinability based upon the elimination of variations in hardness, density, etc.
- (5) The ability to confer consistency and uniformity to large runs of similar parts. These processes can provide very large uniform lots which can be sampled and analyzed with greater significance than with existing processes.

It is apparent to those skilled in the art that various changes and modifications may be made herein without departing from the spirit of the invention or from the scope of the appended claims.

I claim:

1. A method of producing an alloy powder of 5% nickel, 5% copper and 90% refractory comprising the steps of: introducing an aqueous solution of nickel and copper to a dry salt of said refractory; coating refractory particles by continuous blending and evaporation of the

solution, said refractory selected from the group consisting of tungsten and molybdenum; and the step of co-reduction to the alloy metal powder by use of hydrogen or carbon.

2. A method of producing a homogenous alloy powder of a refractory metal-nickel-copper comprising the steps of introducing an aqueous solution consisting of nickel and copper which decomposes at an elevated temperature to a dry salt of refractory metal crystals selected from the group consisting of tungsten and molybdenum, coating said refractory metal crystals with said nickel and said copper by continuous blending and evaporation of said aqueous solution, and co-reducing said coated particles in a reducing atmosphere at a temperature of about 700° to 1100° C., thereby producing a homogenous powder alloy of a refractory metal-nickel-copper.

3. A method of producing a homogenous alloy powder of a refractory metal-nickel-copper comprising the steps of introducing an aqueous solution consisting of nickel and copper ammonia complex which decomposes at an elevated temperature to a dry salt of tungsten crystals selected from the group consisting of ammonium para tungstate and ammonium tungstate, coating said tungsten crystals with said nickel and said copper by continuous blending and evaporation of said aqueous solution, and co-reducing said coated particles in a reducing atmosphere of hydrogen at a temperature of about 700° to 1100° C. thereby producing a homogenous powder alloy of tungsten-nickel-copper.

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L. DEWAYNE RUTLEDGE, *Primary Examiner.*

WAYLAND W. STALLARD, *Assistant Examiner.*