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METHOD OF PREPARATION OF CARBIDES

No Drawing.

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The present invention relates to the preparation of carbides of metals of the sixth group of the periodic system (including tungsten, molybdenum and chromium) with cobalt or nickel, which, according to the information heretofore available, do not readily form a carbide.

The arts have for sometime recognized the fact that carbides of tungsten, molybdenum and chromium were hard, and compositions composed of such a carbide with an admixture of an auxiliary metal such as cobalt, iron or nickel have been suggested for use in making tools and dies. These products are produced by mixing, pressing and sintering the powdered carbide and the powdered metal. The auxiliary metal acts as a cementing agent to support and hold the carbide which, while very hard, is brittle, and alone has insufficient structural strength. The methods heretofore practiced in the preparation of these products have required the comminution of the ingredients to as small a size as possible by mechanical means and the intimate mechanical mixing by grinding of these ingredients.

Cobalt-tungsten carbide has been prepared in accordance with U. S. Patent 1,549,615, British Patent 213,524, and German Patent 420,689, all of which discuss the making of a "hard alloy" of cobalt, nickel or iron with tungsten carbide (having up to 10% binder such as cobalt, 3% to 10% carbon with the remainder tungsten), and the use of such for wire drawing dies. British Patent 251,929 and German Patent 434,527 discuss the use of such tungsten carbide for making cutting and grinding tools containing 10% to 20% of auxiliary metal such as cobalt, with 3% to 10% carbon, the balance being tungsten. It thus appears that cobalt-nickel and iron-tungsten carbide, having up to 20% binder and from 3% to 10% carbon have valuable properties in the manufacture of tools of various sorts.

In tools and dies made according to the methods now available, the quality of the product is dependent to a large extent on the employment of very small particles of binder such as cobalt metal powder and car-

bide such as tungsten carbide, which must be intimately mixed so that the carbide will have been wetted by the binder. Not only must these ingredients be present in condition to be in intimate contact, but it appears that the metal powder used as a binder and the carbide should be free of deleterious foreign substances.

Briefly the preparation of tungsten carbide as heretofore practiced, consists in making pure tungstic oxide, the hydrogen or carbon reduction of the same, and subsequent carburization of the tungsten metal powder produced. Each one of these steps is expensive and the carbide requires grinding to produce small particle size. As regards cobalt metal powder, there are various steps, such as the manufacturing of the oxide of cobalt and the reduction of the same with hydrogen or any other suitable means. The cobalt metal powder is also ground to produce small particle size. The metallic cobalt powder and tungsten carbide are mixed in the correct proportions and ground very intimately. This grinding may be performed in a ball mill, and the mixed powders are screened through an exceedingly fine sieve. These grinding operations both for particle size and mixing are difficult to control, resulting in lack of uniformity and uncertainty of product, and contamination, especially on account of the abrasive action of tungsten carbide. This material is packed into a form under pressure and sintered, as for instance by passing electricity through it.

It is possible to make a series of hard alloys from the various above mentioned carburized metals and binders having varying degrees of hardness and other valuable properties. As an example of the practical application of the invention, I will, however, discuss the same more particularly with respect to the preparation and properties of tungsten carbide-cobalt compositions which may, for convenience, be designated as cobalt-tungsten carbide.

According to the present invention, however, the intimate mixing of the binder with the carbide and the obtaining of very small particles of carbide and binder or auxiliary

metal is secured by a chemical means which necessarily gives greater uniformity than is possible with physical mixing and grinding. That is to say, the auxiliary metal and carburizable metal at no time pass through a state in which an agglomeration of particles of the same material is possible. This obviates much of the fine grinding and intimate mixing. In this manner one is enabled to obtain the resulting product having the necessarily small particle size and intimate mixture without mechanical operations such as grinding.

According to the preferable method of operation, the preparation of the cobalt tungsten carbide is based on the employment of a compound containing both cobalt and tungsten, such as normal cobalt tungstate or cobalt para tungstate, or a mixture of the two. These compounds have definite and well known compositions. As these are chemical compounds rather than mixtures, the ratio of cobalt and tungsten is definite and not changeable and one has an accurate foundation for all calculations.

In making normal cobalt tungstate one may take a 15° Bé. ammonium tungstate solution, which will contain approximately .12 g. of WO_3 per cc. and add thereto the calculated amount of soluble cobalt (such as cobalt chloride, cobalt nitrate, etc.) to form normal cobalt tungstate. The precipitate formed should be washed and dried. To make cobalt para tungstate, one may take a 15° Bé. solution of ammonium tungstate and before adding the soluble cobalt solution, sufficient hydrochloric acid is added at room temperature to produce a solution of ammonium para tungstate. At this point the cobalt chloride solution is added, which throws down a peach colored precipitate of cobalt para tungstate. In this form it can be washed and dried and is thereafter ready for reduction to cobalt-tungsten carbide.

In reducing normal cobalt tungstate, one may take about five to seven parts of the dehydrated powder as indicated above, and mix the same intimately with about one part of carbon in any suitable form. The mix is placed in a graphite crucible or other suitable container. It is convenient to place a graphite disc over the mix and loose lamp-black may be used to cover the disc to prevent oxidation. The crucible is placed in a furnace gradually heated for a period of three hours to bring it to a temperature of about 1,000° C., at which it is held for about five hours. The duration of heating will depend very largely on the dimensions of the crucible or other container, and the quantity of tungstate treated. Less carbon will be required where a strongly reducing atmosphere is maintained in the furnace. Substantially the same procedure may be fol-

lowed in reducing cobalt para tungstate. A reducing and carbonizing gas may be used in place of the solid carbon.

I prefer a minimum temperature to prevent undue sintering. It is, however, possible to employ higher temperatures as long as the cobalt does not become too fluid or the decomposition point of the carbide is not reached.

In carrying out these reducing and concurrent carburization operations, all the carbon apparently unites with the tungsten, forming a tungsten carbide, the cobalt being reduced to the metallic state to provide material for a matrix or binder. This process may be described as a selective carburization, proceeding concurrently with the reduction. It is probable that the matrix forming material thus formed consists of a predominant amount of pure cobalt possibly admixed with varying amounts of tungsten or tungsten and carbon. The amount of carbon used in the reduction of cobalt tungstate is based on the supposition that the tungsten content of the cobalt tungstate is converted to tungsten monocarbide. If the normal and para tungstates are merely dried and not completely dehydrated before reduction, less carbon should be used.

Tungsten forms definite compounds with carbon known as tungsten monocarbide and ditungsten carbide having 6.12% and 3.16%, respectively of carbon. In my researches I have also found that tungsten and carbon form what may be termed carbides, of much higher carbon content, at least as high as 15%. These may be true carbides or mixtures of the same or solid solutions of carbon in some form of tungsten carbide. In these products the carbon cannot be separated out by any of the usual processes employed for separating free carbon from other materials.

The cobalt-tungsten carbides thus produced are in the form of pulverant powders of exceedingly small particle size. This is the result of employing combined cobalt and combined tungsten in the state of molecular subdivision instead of the metallic state. If the optimum temperature has been exceeded, the cobalt-tungsten carbide may be sintered. When normal cobalt tungstate is used as a basic material, there will be 24.2 parts of cobalt to 75.8 parts of tungsten, while the product made from cobalt para tungstate will have 12.1 parts cobalt to 87.9 parts tungsten.

If the desired ratio of cobalt and tungsten in the tool forming material above referred to is 15 cobalt to 80 tungsten, it will be noted that this percentage is intermediate between the percentages obtained when using pure cobalt tungstate and pure cobalt para tungstate. In order to obtain this desired percentage or ratio of cobalt to tungsten, the normal cobalt tungstate powders and the cobalt

para tungstate powders may be mixed in the desired proportions which are about 31 parts normal to 100 parts of para tungstate whereupon the cobalt-tungsten carbide obtained by the reduction and concurrent carburization will have the desired percentage of cobalt.

This process obviates the necessity of making cobalt oxide and the reduction of the same to cobalt metal powder. It also obviates the necessity of making tungstic acid, the reduction of the same to tungsten metal powder and the carburization of the metal to tungsten carbide. In place of these operations in connection with the manufacture of cobalt metal powder and tungsten carbide, this process calls for a single precipitation of cobalt tungstate, the precipitate being easily washed. No amount of mechanical mixing and grinding of cobalt metal powder and tungsten carbide can give the degree of intimacy which is consequent upon the use of cobalt tungstates.

The cobalt-tungsten carbide as prepared is a powder. The particle size is exceedingly small and when the powder is placed in a form and sintered, one obtains a tool having vastly improved properties over tools made from the mechanically produced mixture of cobalt and tungsten carbide. There is a noticeable improvement, especially with respect to the toughness of the tool and its resistance to shock.

As a possible variation of the process above, cobalt oxide and ammonium para tungstate or tungstic acid (H_2WO_4) or tungsten oxide (WO_3) in correct proportions can be intimately ground with carbon and the charge reduced in the same manner as cobalt tungstate. This grinding operation is much less difficult than the grinding necessary where cobalt metal powder and tungsten carbide are employed as raw materials. In case sufficient carbon has been used, the extra carbon of the mix will combine with the reduced tungsten as explained in reducing cobalt tungstate to form tungsten carbide. This process is superior to the process of preparing separately cobalt metal powder and tungsten carbide because some of the necessary operations are obviated by the single reduction of the cobalt and tungsten with the concurrent carburization of the tungsten. It, however, produces the fine particle size as both the cobalt and tungsten were in the state of molecular subdivision.

Inasmuch as 12.1% is the lowest percentage of cobalt to be had from the use of normal cobalt tungstate alone, and certain tools, such as wire drawing dies may employ much lower cobalt content and higher tungsten carbide content, one may obtain such alloys by using the cobalt oxide and tungsten compound mixture, or may dilute the cobalt para tungstate with tungsten as an acid or oxide.

On the other hand, when one desires to exceed the highest percentage (24.2) of cobalt, in the cobalt tungsten carbide, it is possible to employ additional cobalt oxide, or hydrate.

I desire it to be understood that the term cobalt-tungstate when used without qualification is to include normal cobalt tungstate, cobalt paratungstate, or any other cobalt tungstate or mixtures of the various tungstates of cobalt.

I have described the preparation of cobalt-tungsten carbide in considerable detail. The methods employed in making nickel-tungsten carbide, cobalt-molybdenum carbide, nickel-molybdenum carbide, cobalt-chromium carbide, and nickel-chromium carbide, or mixtures of any of these products will, in general, follow the same procedure with such variations in percentages, temperatures and periods of heating as the particular conditions require.

When carbon is used as a reducing agent the auxiliary metal and carbide forming metal are reduced and the latter metal concurrently carburized in the manner above set forth.

Where the metallic constituents are combined with volatile constituents such as oxygen and ammonia, these elements escape during reduction. Where, however, the metallic constituents are combined with non-volatile elements, one should select such raw materials that the foreign matter present in the reduced and carburized product may remain without materially affecting the properties, or may be separated from this cobalt-tungsten carbide by some process which will not decompose the cobalt-tungsten carbide.

I claim:

1. The method of making a carbide composition having at least two metallic constituents, at least one of which forms a carbide while another constituent does not readily form a carbide, which consists in bringing about a close association of all said constituents while in the chemically combined condition, and concurrently effecting a reduction of both constituents and a selective carburization of one of the constituents by carbon, and without fusion or sintering.

2. The method of making a carbide composition having two metallic constituents with only one of which carbon readily forms a carbide, which consists in bringing about a close association of both constituents while each of them is in chemically combined condition, and concurrently effecting a reduction of both constituents and a selective carburization of one of the constituents by carbon, and without fusion or sintering.

3. The method of making a carbide composition having two metallic constituents with only one of which carbon readily forms a carbide, which consists in concurrently re-

- ducing and selectively carburizing a mixture containing both of these metals combined with elements such that the carbide alloy may be separated therefrom the reduction and carburization being carried on at temperatures insufficient to cause fusion.
4. The method of making a carbide composition having two metallic constituents with only one of which carbon readily forms a carbide, which consists in concurrently reducing and selectively carburizing a mixture containing both of these metals combined with volatile constituents the reduction and carburization being carried on at temperatures insufficient to cause fusion.
5. The method of making a carbide composition having two metallic constituents with only one of which carbon readily forms a carbide, which consists in reducing and carburizing a chemical compound including both of said constituents at temperatures insufficient to cause fusion.
6. The method of preparing a carbide composition containing at least two metallic constituents, at least one of which forms a carbide, while another constituent does not readily form a carbide, said alloy having a predetermined relative amount of said two constituents, which consists in preparing a chemical compound including said two constituents, mixing with said compound a compound containing one of said constituents combined with a removable component, and reducing and carburizing the mixture at temperatures insufficient to cause fusion.
7. The method of making a carbide composition having at least two metallic constituents, at least one of which forms a carbide while another constituent does not readily form a carbide, which consists in bringing about a close association of all said constituents, while in the chemically combined condition, with carbon, and reducing the mixture at a temperature at which the non-carburizable metal is converted to the metallic state and the other metal is concurrently reduced and carburized, the temperatures being insufficient to bring about fusion.
8. In the making of cobalt-tungsten carbide compositions, the method which consists in reducing combined oxides of cobalt and tungsten by carbon, and concurrently forming cobalt tungsten carbide, said operation being carried out at temperatures insufficient to cause fusion.
9. The method of making cobalt-tungsten carbide which consists in preparing a mixture of cobalt tungstates, and reducing and carburizing the same at temperatures insufficient to cause fusion.
10. The method of making cobalt-tungsten carbide which consists in reducing and carburizing a mixture of normal cobalt tungstate and cobalt para tungstate at temperatures insufficient to cause fusion.
11. The method of making cobalt-tungsten carbide which consists in reducing and carburizing cobalt tungstate at temperatures insufficient to cause fusion.
12. The method of making cobalt-tungsten carbide which consists in reducing and carburizing cobalt para tungstate at temperatures insufficient to cause fusion.
13. The method of making cobalt-tungsten carbide which consists in reducing and carburizing normal cobalt tungstate at temperatures insufficient to cause fusion.
14. The method of making cobalt-tungsten carbide which consists in bringing about an intimate association of cobalt and tungsten when both are in the chemically combined condition and effecting a simultaneous reduction of both materials and concurrently and selectively carburizing the same without fusion or sintering.
15. The method of making cobalt-tungsten carbide which consists in preparing a mixture of normal cobalt tungstate and cobalt para tungstate, mixing the same with carbon and reducing the mixture at a temperature sufficient to convert the cobalt to metal and concurrently carburize the tungsten but insufficient to cause fusion.
16. The method of making cobalt-tungsten carbide which consists in mixing cobalt tungstate with carbon and reducing the mixture at a temperature sufficient to convert the cobalt to metal and concurrently carburize the tungsten but insufficient to cause fusion.
17. The method of preparing cobalt-tungsten carbide having a predetermined percentage composition of cobalt and tungsten differing from the relative amounts of cobalt and tungsten present in a tungstate of cobalt, which consists in mixing with a selected tungstate of cobalt a compound containing at least one of said metals combined with a removable component, and reducing and concurrently carburizing the mixture.
18. The method of producing a cobalt-tungsten carbide of a desired relative proportion of cobalt and tungsten which consists in mixing together two cobalt tungstates, one having less than the desired percentage of cobalt while the other has more than the desired percentage of cobalt, to produce a physical mixture having an intermediate composition with the desired relative proportion of cobalt and tungsten, and reducing and carburizing the mixture.
19. The method of making cobalt-tungsten carbide which consists in mixing dehydrated cobalt tungstate with carbon, and heating it under reducing conditions at a temperature above 1,000° C. and below fusing temperature.
20. The method of making cobalt-tungsten carbide wherein the desired proportion of cobalt and tungsten is the same as that in a cobalt tungstate, which consists in adding a cobalt salt to a tungstate solution to precipi-

tate such cobalt tungstate, drying the precipitate and mixing it with carbon, and heating the mixture at a temperature sufficient to reduce and concurrently carburize the same and produce metallic cobalt and tungsten carbide and insufficient to decompose said carbide or cause fusion.

Signed at York, in the county of York and State of Pennsylvania, this 4th day of October, 1928.

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