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METHOD OF DISINTEGRATING SINTERED HARD CARBIDE MASSES

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6 Claims

This invention relates to a method of disintegrating sintered hard carbide masses, and more particularly, a method for returning sintered hard carbides back to their presintered particulate form.

Sintered or cemented hard carbides, such as are used in cutting tool bits, dies, wear plates, etc., are generally composed of particles of tungsten carbide bonded together with cobalt. For the so-called steel cutting grades of sintered hard carbides, it is common to also add quantities of titanium carbide and tantalum carbide.

These carbides are relatively expensive materials and therefore, it is highly desirable to recover them from the sintered carbide products, after these products have become worn or broken or otherwise useless, so that the carbides may be reused to form new products. Thus, various methods have been devised in the past for recovering the hard carbides. For example, in the past such carbides have been ground from the original product into small particulate size for reuse. However, such grinding techniques have been slow and cause high wear to the processing equipment. Moreover, the percentage of cobalt mixed with the originally sintered product, remains substantially unchanged, thereby limiting the use of the reground particles, that is, preventing their reuse where sintering with a smaller quantity of cobalt is desired for the new product.

In addition, attempts have been made in the past to, in effect, dissolve the sintered product chemically, such as by the use of various strong acids to attempt to leach out the cobalt and/or chemically dissolve the carbides for reconstituting. Such processes as have been tried, invariably included the use of strong, highly corrosive acids, and high temperatures. Thus, in addition to the disadvantages in handling such a process because of the strongly corrosive acids and high temperatures, which affect equipment being used, etc., there is the additional disadvantage of such processes being extremely slow and thus uneconomical. In addition, such processes have been relatively impractical to use where the sintered carbides are of the steel cutting grades, that is, including titanium carbide and tantalum carbide.

Thus, it is an object of this invention to provide a method for disintegrating sintered hard carbide masses, even of the steel cutting grades, utilizing a weak, non-corrosive acid, low temperatures, and relatively fast operating times, which process will remove substantially all of the cobalt and return the hard carbide particles back to their original, presintered sizes, without substantially affecting the physical characteristics of such particles and thereby permitting their reuse without further processing or chemical treatment.

More particularly, I have discovered that a weak, non-corrosive, phosphoric acid will disintegrate sintered hard carbide masses, dissolving the cobalt and holding the carbide particles in suspension, so that the particles may be mechanically removed, as by centrifuging or filtering, and moreover that this process works best at relatively low temperatures, such as slightly above room temperature, with the recovery rate being many times faster than that believed possible using heated, strong corrosive acids. Moreover, I have discovered that the process may be considerably accelerated by operating first, in an

oxidizing atmosphere of only slightly above atmospheric pressure and additionally accelerated by impacting the sintered masses, preferably by means of autogenous milling caused by rapid vibration of a large number of such masses in a single container.

Thus, with this process, the overall expense of recovering the hard carbides is considerably lower than any of the aforementioned prior art processes making the recovery of such carbides economical and industrially useful, and moreover, eliminating elaborate or expensive equipment, particularly heating equipment, and special container materials for resisting corrosion, etc.

A more complete understanding of the method herein will be obtained from reading the following more detailed descriptions which include comparative data obtained in various tests.

The starting sintered hard carbide material would typically be in the form of a used, worn out or broken tool bit, die part, wear plate or the like which comprises essentially a high percentage of tungsten carbide particles cemented together with cobalt. The particle size may range considerably, but for illustrative purposes may be considered to be in the range of about two microns. Certain of such materials, particularly those used for cutting steel, will also contain titanium carbide and tantalum carbide. Below is a chart illustrating typical examples of starting materials, giving by percentage of total weight, the constituents:

EXAMPLES OF SINTERED HARD CARBIDES

Number	Co	WC	TcC	TaC
(1)-----	8.5	72	8	11.5
(2)-----	4.5	70.7	12.6	12.2
(3)-----	3	93	-----	-----
(4)-----	3	97	-----	-----
(5)-----	6	94	-----	-----

The example indicated by the number (1) above, is normally referred to in industry as "Carbaloy No. 370." This is considered to be one of the most difficult of the sintered hard carbides to disintegrate by any conventional process. Such material was treated by a variety of strong acids, at room temperature, in order to determine the percentage of weight recovery per twenty-four hour period. This is determined by the weight of the sintered object which is disintegrated during each twenty-four hour period of immersion in such acids. During such tests, the container within which a number of such sintered objects were placed, was rotated at a rate of roughly 31-112 r.p.m. in order to agitate in the acid and to make better contact between the acid and the parts of the products. Below is a comparative table showing the results of these various acids and the percent weight recovery.

COMPARISON OF VARIOUS ACIDS, ROTATION (ROOM TEMPERATURE)

No.	Acid	Percentage wt. recovery per 24 hrs.
(1)-----	250 cc., 37% HCl; 60 cc., 35% H ₂ O ₂ -----	13.5
(2)-----	250 cc., 37% HCl; 12 cc., HNO ₃ (70%)-----	7.3
(3)-----	250 cc., 10% HCl; 50 cc., 35% H ₂ O ₂ -----	6.4
(4)-----	10% HNO ₃ -----	4.3
(5)-----	20% HNO ₃ -----	4.8
(6)-----	96% H ₂ SO ₄ -----	4.02
(7)-----	37% HCl, 50 cc.; 200 cc. acetone-----	3.4
(8)-----	10% HNO ₃ -----	3.21
(9)-----	10% HCl-----	3.26
(10)-----	250 cc., 10% HCl; 50 cc. acetone-----	2.67
(11)-----	250 cc., 37% HCl; 50 cc., acetone-----	2.8
(12)-----	70% HNO ₃ -----	2.62
(13)-----	32% HCl-----	2.63
(14)-----	10% H ₂ SO ₄ -----	2.17
(15)-----	20% HCl-----	2.28
(16)-----	10% HNO ₃ -----	3.1
(17)-----	250 cc., 10% H ₃ PO ₄ ; 15 cc., 35% H ₂ O ₂ -----	20.8
(18)-----	10% H ₃ PO ₄ -----	15.1

It will be noted that the percentage of recovery was relatively low, despite the high concentration of corrosive

acids used, except in items Nos. 17 and 18 where weak phosphoric acid was used. In such cases, the recovery rate was many times that of the strong acids, which would be contrary to normal expectations.

Upon further experimentation, I have found that impacting the hard carbide masses during immersion seems to increase the rate of recovery or rate of disintegration. The most practical method discovered by me during these tests for so impacting the parts was by autogenous milling achieved by vibration of the container within which the parts were placed with the acid. For reasons, not known to me, the process seems to be materially speeded up by such method of impacting. For example, below is a comparison chart showing the use of strong acids with vibration which was obtained by placing the hard carbide of the type of Example 1 of above, namely, steel cutting grade "Carbaloy No. 370" in a stainless steel vessel which in turn was vibrated by a vibratory mill at approximately 1450 r.p.m. at 4 mm. amplitude.

COMPARISON OF VARIOUS ACIDS, VIBRATION (ROOM TEMPERATURE)

No.	Acid	Percentage wt. recovery per 24 hrs.
(1).....	10% HNO ₃	8
(2).....	250 cc., 37% HCl; 50 cc., 35% H ₂ O ₂	9.2
(3).....	500 cc., 32% HCl, chlorine gas atmosphere.....	6.8
(4).....	32% HCl.....	4.17
(5).....	10% HCl.....	2.85

It can be seen that in some instances there is a slight increase in the rate of recovery, although in the case of certain acids, such as 10% concentration of HCl, the percentage of increase is very slight. Thus, such vibration with the strong acids still does not yield a commercially economical and useful process.

However, I have discovered that such vibration of the above mentioned phosphoric acid seems to have a considerable affect, far out of expected proportion, in increasing the recovery percentage as indicated by the chart below:

PHOSPHORIC ACID—VIBRATION (ROOM TEMPERATURE)

No.	Acid concentration	Percentage wt. recovery per 24 hrs.
(1).....	5% H ₃ PO ₄	30
(2).....	10% H ₃ PO ₄	32.6
(3).....	20% H ₃ PO ₄	29.2
(4).....	40% H ₃ PO ₄	24.4

As can be seen, using, for example, 10% phosphoric acid and vibrating, as compared to merely rotating for agitation of the acid, approximately doubles the recovery rate.

I have further discovered that, contrary to the prior art techniques, when the method is carried out in an oxygen atmosphere of relatively low pressure, the rate of recovery is increased to some extent and more importantly, is maintained fairly uniformly and seems to maintain the quality of the resultant carbide particles. Below, is a chart indicating the effect of oxygen pressure, utilizing 20% concentration of H₃PO₄, at room temperature with the aforementioned vibration.

EFFECT OF OXYGEN PRESSURE (20% H₃PO₄ AT ROOM TEMPERATURE WITH VIBRATION)

Oxygen pressure (p.s.i.):	Percentage wt. Recovery per 24 hrs.
5	24.5
15	29.2
25	32

Increases in pressure of oxygen seems to have only a slight effect above that of the 25 p.s.i. and the increase pressure results in a slight increase in weight recovery up to about 35 p.s.i. when it tapers off and remains substantially constant at a level slightly above 32% recovery per twenty-four hours.

For optimum results, and particularly in order to maintain the equipment and joints of the equipment leak proof and inexpensive, I have found that 15 p.s.i. seems to give good results for the purposes here.

It was previously believed that by increasing the temperature of the acids used, that any process of the type indicated above, would be accelerated. Contrary to this prior art knowledge, I have found that the temperature used in this process is relatively insignificant and that the yield or recovery seems to decrease, rather than increase, as the temperature increases. Thus, below is a comparative chart showing the effect of temperature in this process.

EFFECT OF TEMPERATURE

(Material, 8.5 Co, 72 WC, 8 TiC, 11.5 TaC; oxygen pressure, 15 p.s.i.; 20% H₃PO₄).

Temperature, degrees centigrade:	Percentage wt. recovery per 24 hrs.
32	32.6
54	32.1
58	32.9
59.5	33.1
39.5	21.4
41	24
45	33.6
4.5	12.6
8.5	9

I have discovered that the most practical operating temperature would be in the range of about 115° F. which is the range of only slightly above room temperature. Since the process generates heat normally, it thus becomes necessary to cool the vessel within which the process was carried out, by simply circulating cooling water around the outside of the vessel to thereby maintain the temperature at roughly room temperature or slightly above room temperature as mentioned above.

As can be seen, the process herein utilizes a weak, substantially non-corrosive acid, at room temperature or slightly above room temperature with a relatively low pressure oxygen atmosphere which is only slightly above atmospheric pressure for practical purposes, so that the equipment needed is highly simplified and the problems of handling the materials is reduced considerably as compared to any use of strong acids or heavy crushing or grinding mills, etc.

The net result of this process is that pieces or chunks of sintered tungsten carbide within which other hard carbides may be mixed and cemented with cobalt, may be disassembled in a relatively short period, without the prior need for mechanically grinding and with the carbide particles in effect returned to their initial size, that is their pre-sintered size. Actually, I have found that the autogenous milling resulting from vibration tends to make the particle sizes even more uniform than they were before sintering.

The cobalt is dissolved in the phosphoric acid and is removed in solution with the acid. The cobalt may then be recovered by various conventional chemical processing to return the cobalt as one product and to recover the acid for reuse. Meanwhile, the carbide particles which normally are of very small size, such as in the order of two microns or thereabouts in typical cutting tools, are suspended in the acid solution from which they may be removed mechanically. Thus, by using a conventional centrifuge or suitable filters, the carbide particles may be removed from the acid which acid may then be chemically treated to remove the cobalt. Thereafter, the acid is available for reuse and the cobalt is available as a byproduct.

The carbide particles are physically the same or essentially the same as they were before the sintering operation took place, that is, they are of essentially the same size and same chemical and physical construction.

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Hence, in essence, the process disassembles the sintered product in the period of roughly three days, as compared to what might otherwise be weeks of incomplete and poor disintegration using prior art methods, and returns the product back into its pre-sintered form. The particles of carbide may then be used as raw material and mixed with the desired amount of cobalt to reassemble a new sintered product.

This invention may be further developed within the scope of the following claims. Accordingly, it is desired that the foregoing description be read as being merely illustrative of an operative embodiment of this invention and not in a strictly limited sense.

Having fully described an operative embodiment of this invention, I now claim:

1. A method of disintegrating sintered hard carbide masses formed of hard carbide particles, such as tungsten carbide, titanium carbide and tantalum carbide, cemented by cobalt, comprising immersing such masses in a relatively weak phosphoric acid at relatively low temperature, such as in the range of slightly above room temperature, thereby causing the cobalt to dissolve in said acid and freeing the particles in essentially their original, pre-sintered sizes, from the masses and causing the particles to suspend in the acid; and thereafter mechanically separating the particles from the acid, such as by centrifuging or filtering.

2. A method as defined in claim 1 and including autogenously milling such said masses while they are immersed in said acid.

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3. A method as defined in claim 1 and including vibrating said masses to cause them to rapidly impact against each other, for thereby autogenously milling said masses, while they are immersed in said acid.

4. A method as defined in claim 1 and said acid being concentrated in the approximate range of 5-40% phosphoric acid to water.

5. A method as defined in claim 1 and including enclosing said masses and acid in a sealed container and maintaining an oxygen atmosphere in said container of approximately 5 to 50 p.s.i.

6. A method as defined in claim 1 and including subjecting the mixture of such masses and phosphoric acid to oxygen by means of adding a relatively small quantity of hydrogen peroxide to said acid.

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