United States Patent

[11] 3,595,484

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[21] Appl. No. **803,323**
[22] Filed **Feb. 28, 1969**
[45] Patented **July 27, 1971**
[73] Assignee **The United States of America as represented by the Secretary of the Interior**

[54] RECLAMATION OF REFRACTORY CARBIDES FROM CARBIDE MATERIALS

6 Claims, 1 Drawing Fig.

[52] **U.S. Cl.** **241/3,** 75/0.5, 75/213, 241/23
[51] **Int. Cl.** **B02c 19/12**
[50] **Field of Search** ..... 241/1, 3, 20, 23, 29; 75/0.5, 211—213, 204, 203, 170—1, 174, 175.5; 23/208, 309—312

[56] **References Cited**

UNITED STATES PATENTS

3,515,540	6/1970	Meadows	75/0.5

FOREIGN PATENTS

582,921	12/1946	Great Britain	241/3

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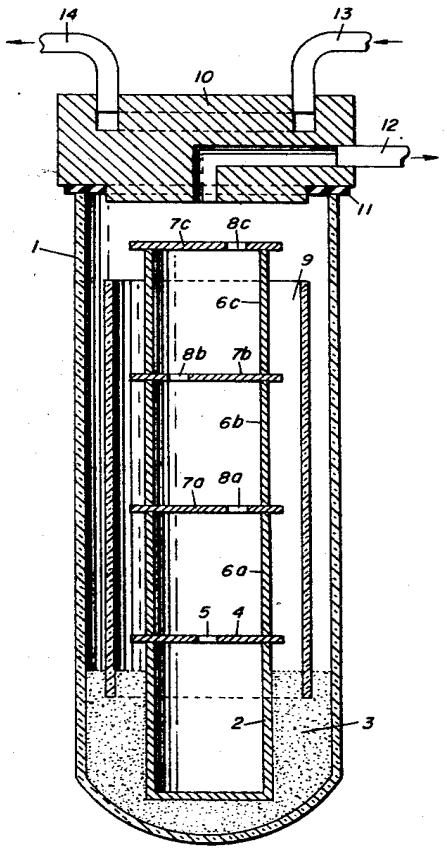
ABSTRACT: Refractory carbides, particularly tungsten carbide, are reclaimed from cemented carbides by treating the cemented carbide with molten zinc and subsequently distilling the zinc from the mass. The zinc forms an alloy with the cementing agent, usually cobalt, thereby dissolving the carbide-cementing agent bond and permitting recovery of a mixture of the carbide and the cementing agent in a form that can be reused in preparation of cemented carbides.



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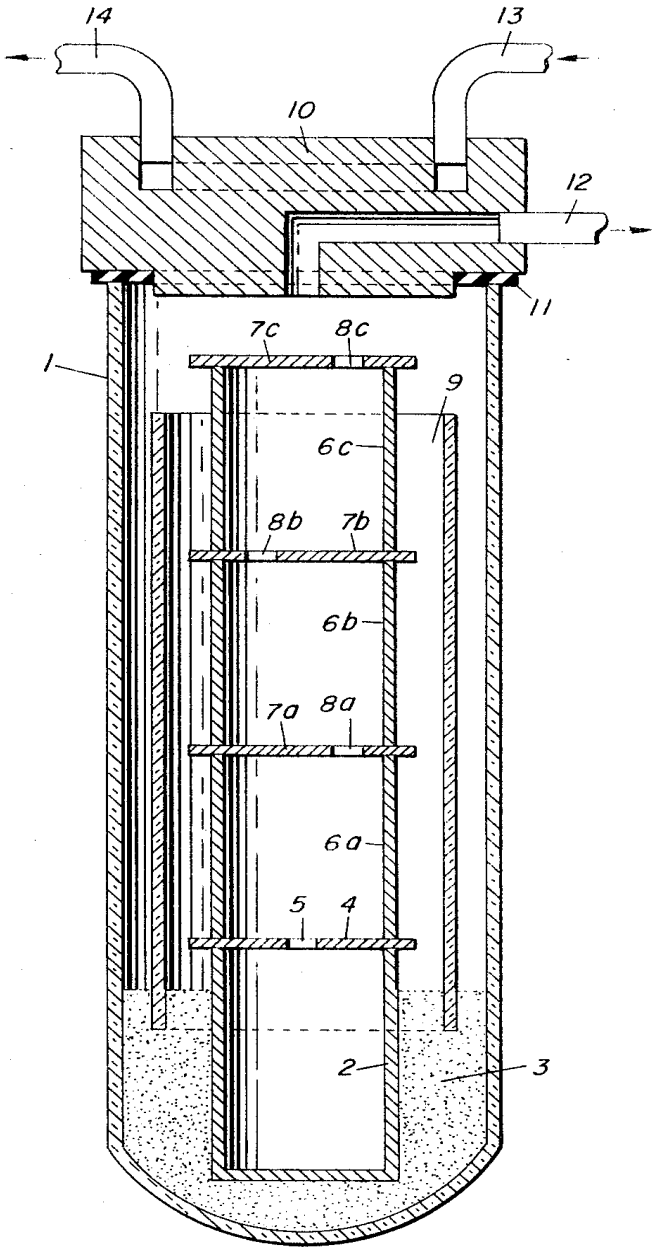

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RECLAMATION OF REFRACTORY CARBIDES FROM CARBIDE MATERIALS

This invention relates to recovery of refractory carbides, such as tungsten, titanium, tantalum and niobium from cemented carbides. The cemented carbides are conventionally prepared by mixing the carbide powder or powders with about 5 to 15 percent of cobalt or nickel powder which acts as a cementing agent when the product is sintered. The result is a cemented carbide that approaches the diamond for hardness. Because of this hardness tungsten carbide is widely used as a material for insert bits used in rock drilling, in tools for cutting cast iron, nonferrous metals, etc., and in dies for drawing wire, bar or sheet metal. Highly alloyed steel cutting grades usually consist largely of tungsten carbide with additions of titanium or tantalum carbide.

The cemented carbides are made industrially by high-pressure compacting of refractory carbide powders with the binder (usually cobalt powder) and sintering the compact below 1,000° C. in a nonoxidizing atmosphere. This compact is relatively soft and can be machined to required shape and dimensions before the compact is resintered at about 1,400° C. in hydrogen to produce optimum desirable properties.

Appreciable reject scrap is generated during the processing because of cracks, chips in tool cutting edges, or the tools not meeting desired dimensions or specifications, etc. Used carbide scrap also accumulates from industrial use and can be returned for reclamation. High expense is encountered in reclaiming the carbide scrap due to difficulty in either grinding or removing the cobalt binder to loose the carbide particles. Normally, in a carbide tool, a thin film of cobalt coats each carbide particle and also cements the particles together after fusion of these films. The carbide fraction of the reject scrap could be reused if the cobalt bond could be removed, but conventional methods of dissolving the cobalt will only slowly dissolve it over a period of many weeks.

It has previously been found, as disclosed in British Pat. No. 582,921, that the refractory carbides may be recovered from the scrap material by treatment of the scrap with molten zinc to form an alloy of the zinc and the cementing agent, e.g., cobalt. This alloy is then removed by dissolving in dilute acid. This dissolution with acid, however, constitutes a relatively expensive and time consuming operation since a large volume of acid and a leaching time of about 24—30 hours is required. Furthermore, the resulting solution must be treated to recover the zinc and cobalt, and the remainder of the leach solution becomes a waste problem. In addition, this method requires additional equipment for the leaching operation and also for filtering and drying the product carbides.

It has now been found, according to the process of the invention, that recovery of the refractory carbide, as well as the cementing agent, from the cemented carbide may be accomplished rapidly and economically by treating the cemented carbide with molten zinc, followed by distillation of the zinc from the mixture at elevated temperature and under reduced pressure (vacuum). Treatment with the molten zinc, which results in formation of a molten alloy with the cementing agent, has been found to break the bond between the carbide and the cementing agent. Hence, when the zinc is removed from the mixture by distillation the resulting product consists of a mixture of the carbide and the cementing agent in which the bond between the two is broken. The mixture is, therefore, readily ground to a powder of a particle size similar to that of the original carbide and cementing agent, i.e., about ½ to 1 micron, and reused in preparation of the cemented carbide without further processing or additives. The zinc vapors are also readily recovered by condensation in a cooler zone of the furnace used in the distillation. The process of the invention is, therefore, unique in that virtually all components are recovered and can be reused without any waste products.

The drawing illustrates, in cross section, one specific embodiment of an apparatus suitable for use in the method of the invention. This apparatus comprises a quartz vacuum tube **1** containing carbon crucible **2** imbedded in dried MgO sand **3**. Crucible **2**, in which the carbide is treated with the molten zinc, is covered by carbon plate **4** having hole **5** in the center thereof. Carbon sleeves **6***a*, **6***b* and **6***c* are located vertically above crucible **2** and plate **4** and are separated by carbon plates **7***a* and **7***b*. Carbon plate **7***c* covers the top of sleeve **6***c*. Plates **7***a*, **7***b* and **7***c* have holes **8***a*, **8***b* and **8***c* therethrough and located off center. These plates provide surfaces for condensation of the zinc vapor as it is distilled from crucible **2**. Quartz sleeve **9** surrounds the major portion of the combination of crucible, sleeves and plates and serves to prevent the zinc vapors from condensing on the inside of vacuum tube **1**. Stainless steel vacuum head **10** is fitted to the top of vacuum tube **1** via rubber gasket **11**. Head **10** is provided with a vacuum line **12** and with water inlet and outlet lines **13** and **14** for water-cooling of the head.

The apparatus employed is conventional distillation apparatus and many possible modifications will be apparent to those skilled in the art. For example, for large scale industrial application the furnace could be modified by attaching a condensing chamber on the side of the furnace and controlling the temperature of this chamber to permit the zinc vapors to condense to liquid zinc which could be tapped before the reclaimed carbides and cobalt were cooled to room temperature. Heat required for the process of the invention is supplied to the apparatus by means of any conventional means such as resistance-heating using electrical energy.

The weight ratio of the zinc used in the process of the invention to cobalt or nickel in the cemented carbide will usually range from about 30:1 to 10:1, with a range of about 20:1 to 15:1 being preferred. The temperature employed in the treatment with molten zinc will range from about 750° to 850° C., with a temperature of about 800° C. usually being optimum. Time required for the treatment with the molten zinc is dependent on the size and shape of the scrap objects and will range from about 2 to 4 hours, with about 2 hours usually being sufficient for smaller items. The zinc treatment is preferably carried out in an inert atmosphere such as helium, nitrogen, or argon.

Removal of the zinc is then accomplished by distillation at a temperature of about 600° to 850° C., preferably about 800° C., under a pressure of about 1 to 100 microns, preferably about 10 to 50 microns. Removal of the zinc is usually complete in about 6 to 8 hours, about 6 hours usually being sufficient. The resulting, usually spongy, product is then cooled to room temperature, preferably in an inert atmosphere such as helium to avoid any possibility of oxidation. This product, which contains virtually all of the refractory carbide and the cementing agent, is recovered in a mass which is brittle and can be readily ground to a powder of the original particle size of about ½ to 1 micron for reuse in preparation of cemented carbides.

The following examples will illustrate the invention:

EXAMPLE 1

The apparatus employed was of the type shown in the drawing and was heated by electrical resistance. 450 grams of cemented carbide reject scrap having a particle size of ½ to 1 micron and a composition of 94 percent tungsten carbide and 6 percent cobalt were treated with an equal weight of zinc at 800° C. for 2 hours in an atmosphere of helium (provided via vacuum line). The zinc was then distilled off in 6 hours at 800° C. under a pressure of 10—50 microns. The zinc vapors were collected in the cooler portion of the furnace, resulting in 99.9 percent recovery of the zinc.

The resulting spongy carbide-cobalt product was then cooled to room temperature in vacuo to yield a brittle mass containing substantially all of the original tungsten carbide and cobalt contents. This mass was readily ground to a particle size of ½ to 1 micron and all material could be reused directly in the preparation of a cemented carbide.

EXAMPLE 2

In this example the procedure and results were essentially the same as those of example 1, except that the cemented carbide reject scrap consisted of 72 percent tungsten carbide, 12 percent tantalum carbide, 8 percent titanium carbide and 8 percent cobalt.

What we claim is:

1. A method for reclaiming refractory carbides from cemented carbides comprising treating the cemented carbide with molten zinc for a time and at a temperature sufficient to form an alloy of the zinc and the cementing agent, and subsequently distilling the zinc from the resulting mass.

2. The method of claim 1 in which the refractory carbide consists essentially of tungsten carbide.

3. The method of claim 1 in which the cementing agent is cobalt.

4. The method of claim 1 in which the temperature and time of the treatment with molten zinc are about 750° to 800° C. and 3 to 2 hours, respectively.

5. The method of claim 1 in which the distillation of the zinc is carried out at a temperature of about 700° to 800° C. and under a partial vacuum of about 10 to 50 microns.

6. The method of claim 1 in which the resulting mass is subsequently cooled to room temperature in an inert atmosphere or in a vacuum and then ground to a powder for reuse in preparation of a cemented carbide.

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