

UNITED STATES PATENT OFFICE

2,407,752

PROCESS OF SEPARATING HARD CONSTITUENTS FROM SINTERED HARD METALS

Edward Moor Trent, Coventry, England, assignor to Powderloys Limited, Coventry, England, a British company

No Drawing. Application September 5, 1945, Serial No. 614,601. In Great Britain October 4, 1944

6 Claims. (Cl. 23—208)

1

This invention is concerned with the recovery of hard constituents from sintered hard metals, and in particular with the recovery of tungsten carbide and other hard carbides from hard metal scrap.

The so-called sintered hard metals, known also as cemented carbides, comprise sintered compositions of one or more metallic carbides, usually the carbides of tungsten, titanium, tantalum and niobium, with an auxiliary binding metal of the iron group, usually cobalt and less generally nickel. One well known composition comprises tungsten carbide particles, the size of which is of the order of .002 mm., bonded together with 6 per cent of cobalt by sintering in known manner, but the amount of cobalt may vary from say 5 up to about 15 per cent.

A considerable amount of scrap of the hard alloys is inevitably produced and it is desirable to recover the valuable constituents of this scrap.

Methods of recovery depending on mechanical disintegration and reduction to a powder are difficult because of the hardness of the carbide and the fineness to which it must be reduced so as to be ready for use in making fresh sintered products. The carbide should be reduced to a powder of grain size not greater than about .005 millimetre, since the grains of carbide in the sintered product are usually smaller than this, of the order of .002 millimetre. It is possible to recover the carbide from scrap materials by chemical processes using strong acids which attack the cobalt but which do not attack the carbide or only to a small extent, but such processes are not economical because of the long time required and the difficulties involved in handling the strong acids which must be used.

I have now discovered that it is possible to accelerate the process of separation, and to render the use of strong acid unnecessary, by first causing another metal, namely zinc, to alloy with the auxiliary binding metal such as cobalt at an elevated temperature above the melting point and below the boiling point of the other metal, allowing the product to cool, and then dissolving the alloy formed between the added metal and the auxiliary binding metal with dilute acid. The hard carbide particles are unaffected by this process and can then be recovered from the residue. The added metal and the auxiliary metal can be recovered from the solution if desired.

The metal which is used to form an alloy with the auxiliary bonding metal of the sintered hard metal should have the following desirable properties: it should readily form an alloy with the

2

said auxiliary bonding metal; it should have a melting point which is not greatly in excess of 1100° C., otherwise expensive heating furnaces are required to attain the necessary temperature; it should have a boiling point not appreciably less than 800° C., otherwise the maximum temperature which can be used in heating may be too low to give rapid alloying of the metal and the auxiliary bonding metal; it should not be a very expensive or rare metal; and it should give an alloy with the auxiliary bonding metal which is easily dissolved in acids. I have found that zinc fulfills these requirements, and no other common or inexpensive metal does so, but alloys consisting mainly of zinc can be used.

Molten zinc attacks the auxiliary metal of sintered hard metals very rapidly particularly at temperatures from 600° C. to 800° C. and above. The rate of attack increases with the temperature. The molten zinc alloys with the cobalt or nickel and provided the proportions are correct the alloy so formed should be molten at the treatment temperature.

The melting point of cobalt-zinc or nickel-zinc alloys rises rapidly as the cobalt or nickel content increases. An alloy of 10% cobalt and 90% zinc melts at about 300° C., and one with 20% cobalt and 80% zinc at about 900° C. As the temperature to be used should be well below the boiling point of zinc, which is at about 907° C., the cobalt-zinc alloy formed should contain not more than 10% cobalt if it is to remain molten at the treatment temperature. Thus the quantity of zinc used should preferably be at least ten times the weight of cobalt in the sintered hard metal being treated. Similarly, when nickel is used as the bonding metal, the weight of zinc should also preferably be at least ten times the weight of nickel in the sintered hard metal being treated.

In practice the proportion of zinc to auxiliary metal may be considerably higher, and assuming the percentage of binder in the sintered hard metal to be from 6 to 12, the weight of zinc used should not be less than 0.6 to 1.2 times the weight of the hard metal depending on the composition.

The acid used to decompose the products of the melt and to dissolve the alloy formed between the zinc and the auxiliary metal should be one which rapidly attacks the alloy but which is not strongly oxidising since such oxidising acids also attack tungsten carbide and other hard metal carbides as is well known. For example, strong nitric acid is not suitable.

I have found that sulphuric acid of a strength of 20 per cent of concentrated acid to 80 per cent

of water by weight, or thereabouts, is convenient, and this acid attacks the zinc-containing alloy rapidly, but does not attack the hard carbide particles. Of course, other acids and other concentrations of sulphuric acid could be used, except that the concentration of sulphuric acid should not be much greater than 30 per cent, otherwise the sulphates formed by the reaction do not remain in solution.

In carrying the invention into effect, the metal pieces are coarsely crushed or broken into fragments, preferably not thicker than $\frac{1}{8}$ inch to facilitate alloying, and are placed in a crucible with granulated zinc in an amount about $1\frac{1}{2}$ times the weight of the hard metal to be treated. Preferably charcoal or a suitable flux is added to prevent undue oxidation of the zinc. The contents of the crucible are raised to a temperature of about 800° C., and maintained at that temperature for about one to two hours. The zinc may be melted first if preferred and the crushed hard metal scrap material is then added to the melt and covered with the charcoal or flux.

The melt may be allowed to solidify in the crucible or may be poured into moulds. In either case it should be broken into pieces of one or two inches in size. Alternatively, the melt may be granulated by pouring it into water, and when this is done, crushing is not necessary. The product of the melt, consisting of an alloy of zinc and the auxiliary binding metal together with particles of hard carbide, is then treated with sulphuric acid diluted to about 20 per cent strength by weight until all reaction ceases. To ensure complete solution of the zinc-containing alloy in the form of sulphates excess of the acid should be used. The reaction takes place more rapidly if the solution is warm, and a convenient way of effecting this is to put the products of the melt into cold water and to add concentrated sulphuric acid until the required concentration is obtained. The heat evolved by diluting the concentrated acid raises the temperature to such a degree that the reaction proceeds rapidly, and the heat of the reaction maintains the temperature.

The cobalt and zinc can of course be recovered from the solution by known methods. The particles of hard carbide are practically unaffected by the acid treatment and, after they have settled, the solution of sulphates is decanted off. The hard carbide particles which remain behind are thoroughly washed with water to remove all salts and acid, using distilled water for the last washing operation, and the particles are then dried under such conditions that no appreciable oxidation takes place, for example in a vacuum oven. Sieving is preferably employed to remove any particles exceeding the size of the original tungsten carbide particles, which larger particles may comprise any incompletely treated hard metal or impurities accidentally included. The sieved hard carbide particles may now be used for incorporation in sintered hard metal in known manner.

When sintered hard metal containing carbides of two or more metals is so treated, the recovered carbide particles are in substantially the same proportions as were included in the untreated hard metal and the particles are generally of the same size as in the composition before treatment. Hence, the separated hard carbide product is suitable for use in making fresh hard metal alloy of similar composition.

As an example of the process according to the invention, the following may be given:

Zinc weighing $1\frac{1}{2}$ kilograms was melted in a salamander crucible in an electric furnace and the surface of the melt was covered with wood charcoal. One kilogram of scrap sintered hard metal of an average composition of about 88 per cent tungsten carbide and 12 per cent cobalt was added, and the temperature was maintained at 775° to 800° C. for $1\frac{1}{2}$ hours. The crucible was covered with a graphite lid, and the melt was stirred at intervals of $\frac{1}{2}$ hour. At the end of the heating period the melt was poured into water, and the charcoal was washed off. The product of two such melts, that is from the treatment of 2 kilograms of scrap hard metal, was placed in a porcelain vessel of 20 litres capacity, 12 litres of tap water were added, and 3 kilograms of concentrated sulphuric acid were poured in sufficiently rapidly to maintain the temperature at about 70° C. The reaction was allowed to proceed overnight, and the next morning the liquid was siphoned off, and a small amount of water and acid were added to ensure completeness of the reaction. After decanting off the acid, the particles were sieved wet through a 100 mesh sieve, and the fine particles which passed through the sieve were washed with 5 per cent sulphuric acid, then 8 times with tap water, and finally twice with distilled water. The particles were then centrifuged to remove excess water, and dried in a vacuum oven. Tungsten carbide recovered from scrap in this manner was made into sintered hard metal by adding 12 per cent of cobalt in known manner, and the product was substantially of the same quality as the hard metal from which the carbide was recovered.

I claim:

1. A process of recovering hard metal carbides from scrap material comprising hard metal carbides and an auxiliary metal of the iron group, in which process coarsely crushed scrap material is fused with zinc to form alloy of zinc with the said auxiliary metal, the product being cooled and the alloy removed by a solvent therefor, followed by washing leaving behind the hard carbide particles.

2. A process of recovering hard metal carbides from scrap material comprising hard metal carbides and an auxiliary metal of the iron group, in which process coarsely crushed scrap material is fused with zinc to form alloy of zinc with the said auxiliary metal, the proportion of zinc used being sufficient to form with the auxiliary metal an alloy containing not more than 10% of the auxiliary metal, the product being cooled and the alloy removed by a solvent therefor, followed by washing leaving behind the hard carbide particles.

3. A process of recovering hard metal carbides from scrap material comprising hard metal carbides and an auxiliary metal of the iron group, in which process coarsely crushed scrap material is fused with zinc to form alloy of zinc with the said auxiliary metal, the product being cooled and the alloy removed by a solvent therefor, consisting of diluted sulphuric acid, followed by washing leaving behind the hard carbide particles.

4. A process of recovering hard metal carbides from scrap material comprising hard metal carbides and an auxiliary metal of the iron group, in which process coarsely crushed scrap material is fused with zinc to form alloy of zinc with the said auxiliary metal, the product being cooled and

5

the alloy removed by a solvent therefor consisting of sulphuric acid diluted in the ratio of about twenty per cent by weight of acid to eighty per cent of water, followed by washing leaving behind the hard carbide particles.

5. A process of recovering hard metal carbides from scrap material comprising hard metal carbides and an auxiliary metal of the iron group, in which process coarsely crushed scrap material is fused with zinc to form alloy of zinc with the said auxiliary metal, the product being cooled and the alloy removed by a solvent therefor, followed

6

by washing several times in tap water and finally in distilled water, leaving behind the hard metal carbides from which water is removed by centrifuging followed by drying.

5 6. A process of recovering hard metal carbides from scrap material in accordance with claim 1, wherein the auxiliary metal consists particularly of cobalt, and the amount of zinc added is sufficient to form with the cobalt an alloy containing not more than 10% of cobalt.
10

EDWARD MOOR TRENT.