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TUNGSTEN CARBIDE PURIFICATION

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This invention relates to reducing the trace metal content of tungsten carbide. More particularly, this invention relates to a refining process for reducing the trace metal content, such as iron and manganese, of tungsten carbide which comprises heating a mixture of tungsten carbide and an alkali metal pyrosulfate salt to a temperature where the salt component is molten.

Tungsten carbide is an extremely important article of commerce, useful in applications requiring high temperatures, hardness and/or high wear resistance. It is the most important constituent of modern cemented carbides. Sintered or fused tungsten carbides are employed in applications requiring high wear resistance.

Tungsten carbide is well known and can be prepared, for example, by those methods described in "Refractory Hard Metals" by Schwarzkoff et al., pp. 138–161 (MacMillan Co., 1953). However, tungsten carbide produced by these methods does not always meet specifications as to trace metals, for example, iron and manganese, present in the final product. Thus, where tungsten carbide is prepared by the method of Li and Dice, described in U.S. Patent 2,535,217, wherein the carbide is produced directly from ore containing tungsten oxide by reduction with carbon, such as bituminous coal, in the presence of iron-tin alloys at temperatures as low at 1420° C., there is obtained a product containing iron and manganese in the order of about 1 or more percent. These trace metals, which tend to soften the carbide, cannot be removed even when tungsten carbide is treated with strong acids under conditions at which chemical attack of the tungsten carbide itself is observed. Thus, it appears that these trace metals are trapped in the carbide in such a manner that is resistant to chemical attack.

Unexpectedly, I have now discovered that the amount of trace metals, such as iron and manganese, present in tungsten carbide can be reduced, for example, to 20–30% of their original content by a process which comprises heating a mixture of tungsten carbide and a pyrosulfate salt, for example, an alkali metal pyrosulfate, to a temperature where the salt is molten. The unexpectedness of this process is enhanced by the fact that removal is effected by this process whereas strong acid extractions fail under extreme reaction conditions.

The mechanism of the reaction is not understood since if the trace metals were on the surface of the crystals of carbide, one would expect them to be removed by acids. Since this is not the case, the trace metals are probably trapped in the interior of the crystals. On the other hand, if this is true, it is difficult to conceive of a mechanism whereby reaction with a pyrosulfate salt should succeed where strong acid treatment fails.

In general, the reaction is carried out by heating a mixture of tungsten carbide particles and an alkali metal pyrosulfate, for example, potassium pyrosulfate, for 5 minutes to two hours or longer, but preferably from 10 to 20 minutes, at a temperature where the pyrosulfate component is molten, cooling, and then extracting the

fused mixture with water. Further purification can be effected by washing with a basic solution, such as ammonium hydroxide, and subsequently washing with a dilute acid, such as hydrochloric acid, followed by a water wash.

The ratio of tungsten carbide to the pyrosulfate salt is not critical provided there is sufficient pyrosulfate salt to stoichiometrically react with the trace metals present in the carbide. There is no upper limit to the amount of pyrosulfate required except that based on practical considerations. In practice, I have employed 1–20 parts or more of potassium pyrosulfate for each part by weight of carbide. Although the temperature of the reaction mixture is not critical provided the reaction mixture is fused, in practice I have employed temperatures of from 300 to 500° C. or higher, preferably about 350° C.

In addition to adding pyrosulfates to tungsten carbide, ingredients may be added which are capable of forming pyrosulfates in situ. Thus, potassium hydrogen sulfate or potassium sulfate moistened with sulfuric acid mixed with tungsten carbide forms potassium pyrosulfate in situ during heating. In addition an excess of the sulfate, bisulfate salt or sulfuric acid lowers the melting of the fused mixture so that mixtures employed in the process can be fused below the melting point of potassium pyrosulfate itself, for example, below 300° C.

The following examples are illustrative of the practice of my invention and are not intended for purposes of limitation. In the examples, all parts are by weight unless otherwise stated.

The following examples illustrate the reduction of the iron and manganese content of tungsten carbide. In the following example, 2 parts of potassium pyrosulfate ($K_2S_2O_7$) and 1 part of tungsten carbide particles were intimately mixed and heated as shown in Table I. When the resulting melts had cooled to room temperature, they were dissolved in water and treated with concentrated ammonium hydroxide. The resulting tungsten carbide crystals were then separated by filtration, and washed with dilute hydrochloric acid and water. The starting materials and products were analyzed for iron and manganese by X-ray emission spectroscopy. These results are presented in Table I.

TABLE I

Potassium pyrosulfate fusions of tungsten carbide

Example	Reaction Conditions	Original Iron and Manganese Content in Percent	Percent of Original Trace Metal Remaining	
			Fe	Mn
1	40 min. at 350° C	1.08	21	27
2	10 min. at 400° C	1.08	18	30

Although the foregoing examples have described a few variations and modifications of ingredients and reaction conditions which may be employed in the practice of the present invention, it should be understood that my process is also applicable to other reaction conditions, and proportions of ingredients which are not specifically illustrated by the examples. For example, other fusable pyrosulfate salts, such as sodium pyrosulfate, etc., can also be employed.

The products of this invention are useful in these applications for which tungsten carbide is now presently used, taking into consideration that the reduction of the iron and manganese content produces a harder material. Thus, the product of my invention can be used in tools, crucibles, machinery, drilling apparatus and other applications which demand refractory properties, hardness and/or high wear resistance.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A process for removing from impure tungsten carbide particles, the trace metals which react with molten alkali metal pyrosulfates, which comprises contacting the impure tungsten carbide with a molten alkali metal pyrosulfate, thereby extracting the trace metals into the molten salt and thereafter separating the purified tungsten carbide from the fusion mass.

2. The process of claim 1 wherein the pyrosulfate salt is potassium pyrosulfate.

3. The process of claim 1 where the reaction product is extracted with water.

4. The process of claim 2 where the reaction product is extracted with water.

5. The process of claim 4 where water-extracted tungsten carbide is treated first with a base, then with an acid, and thereupon washed with water.

6. The process of claim 1 wherein the impure tungsten carbide is a tungsten carbide resulting from the reduction of tungsten oxide ore with carbon.

7. A process as in claim 6 wherein the pyrosulfate salt is potassium pyrosulfate.

8. The process as in claim 7 wherein the fusion mass is extracted with water and the separated tungsten carbide is treated first with a base, second with an acid, and third with water.

9. The process as in claim 8 wherein the base is ammonium hydroxide and the acid is hydrochloric acid.

No references cited.