

## UNITED STATES PATENT OFFICE

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## PROCESS FOR MAKING TUNGSTEN MONOCARBIDE FROM TUNGSTEN-CONTAINING MATERIAL

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This invention relates to an improved process for making tungsten monocarbide from tungsten-containing material and has to do, more particularly, with a process by which tungsten monocarbide (WC) may be made directly from tungsten-containing ore, or other tungsten-containing material.

Heretofore, the manufacture of tungsten carbide has required that the tungsten-containing ore be smelted to produce tungsten metal, or converted to tungsten oxide, and such tungsten powder, or powdered tungsten oxide, has been mixed with carbon and heated, at a temperature and for a length of time, sufficient to cause carburization of the tungsten metal. This product may vary somewhat in carbon content from the theoretical carbon content of 6.12%, and sometimes contains free carbon, depending upon the care taken in the carburizing process.

The principal object of my invention is to provide a process for making tungsten monocarbide from tungsten-containing ore, or other tungsten-containing material, which is efficient and economical, being comparatively simple and inexpensive to perform and giving a relatively high recovery.

Another object of my invention is to provide a process for making tungsten monocarbide directly from tungsten-containing ore, or other tungsten-containing material, which gives, as a resulting product, a tungsten monocarbide of uniform carbon content and density and substantially pure.

Further objects, and objects relating to details and economies of operation, will definitely appear from the detailed description to follow. In several instances, I have accomplished the objects of my invention by the means described in the following specification. My invention is clearly defined and pointed out in the appended claims.

In general, my invention consists in preparing a charge including the tungsten-containing material or ore, silicon and carbon, heating this charge to a temperature above 2000° C., cooling the resulting regulus, leaching the regulus material with acids to remove the acid-soluble portions thereof and, then, subjecting the remaining undissolved portion to gravity separation, by means of which a light portion, relatively low in density, is separated from a heavy portion, relatively high in density. This heavy portion consists substantially of tungsten monocarbide (WC). The silicon is preferably added to the charge in the form of silica (SiO<sub>2</sub>) and should amount to at least 4% of the weight of the ore or tungsten-containing material. The carbon added to the charge should

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amount to at least 10% of the weight of ore or tungsten-containing material. Furthermore, the charge may be heated in a graphite crucible, which may furnish additional carbon to the molten mass. I have found it desirable to maintain the charge at a temperature of about 2500° C. for about three hours.

It is essential that the charge should include a metal, such as iron, manganese, nickel or cobalt, capable of combining with carbon to form carbides having melting points much lower than the melting point of tungsten monocarbide (WC), and also capable of forming compounds with silicon. In many instances, the tungsten-containing ore will include such a metal and, in that case, the charge may consist merely of the ore, silica and carbon. However, where the tungsten-containing ore or material does not include such metal, it should be added as a part of the charge.

The principal sources of tungsten are the ores known as wolframite, hubnerite and scheelite. Wolframite is principally an iron manganese tungstate (Fe, Mn) WO<sub>4</sub>. Hubnerite is principally manganese tungstate (MnWO<sub>4</sub>) and scheelite is principally calcium tungstate (CaWO<sub>4</sub>). I have found that my process is applicable to the production of tungsten monocarbide (WC) directly from any of these ores.

The following examples state the procedure followed by me, in several instances, in successfully carrying out the process of this invention.

## Example 1

A charge was made up consisting of 90 pounds of wolframite, containing 73% of tungsten trioxide (WO<sub>3</sub>), 12 pounds of silica (SiO<sub>2</sub>) and 12 pounds of carbon. This charge was placed in a graphite crucible and heated to a temperature of from 2000° C. to 2400° C., several hours being consumed in bringing the charge up to the maximum temperature, at which it was maintained for three hours. The crucible and its contents were then permitted to cool, the crucible was broken and the contents were removed and broken up in a jaw crusher to pieces less than a quarter of an inch in size. These pieces were then subjected to treatment in an acid bath of hot muriatic acid (30% HCl) to which there was added a slight amount of oxidizing agent, such as, 5% of nitric acid, in cases where the material was not attacked sufficiently by muriatic acid alone. Other acids, such as dilute sulphuric acid may be used instead of muriatic acid. Portions of the regulus material are dissolved by this treatment and removed by decanting the acid bath.

This treatment also disengages the light metallic silicides formed. The residue is subjected to slight attrition, as in a ball mill, for the purpose of further disengaging, from the heavy insoluble material, particles of light impurities such as silicides and silicates adhering thereto. The residue may be subjected to further acid treatment if desired. The remaining undissolved material is then subjected to gravity separation, as by panning, or on a well-known type of gravity concentration table. The insoluble residue is thus separated into two portions, a light portion, and a heavy portion, the former having a density approximately one-third that of the latter, which is substantially pure tungsten monocarbide (WC). Having subjected the regulus, resulting from the heating of the charge described, to the treatment above referred to, there was recovered a heavy portion consisting of 42.9 pounds of tungsten monocarbide (WC), the carbon content of which was 6.10%. Of the tungsten contained in the charge, 77.3% was recovered as tungsten monocarbide.

#### Example 2

A charge was made up consisting of 3300 grams of wolframite (containing about 73%  $\text{WO}_3$ ), 1000 grams of nickel, 750 grams of manganese dioxide ( $\text{MnO}_2$ ), 150 grams of silica ( $\text{SiO}_2$ ) and 600 grams of carbon. This charge was heated in a graphite crucible, at the same temperature and for the same time as described with reference to Example 1, and afterwards subjected to acid leaching and gravity separation, as described above. In this instance, the heavy portion recovered consisted of 1465 grams of tungsten monocarbide (WC), having a carbon content of 6.19%. Of the tungsten present in the charge, 71.3% was recovered as tungsten monocarbide. Cobalt may replace nickel in the charge.

#### Example 3

A charge was made up consisting of 3300 grams of hubnerite ( $\text{MnWO}_4$ ), 1000 grams of nickel, 150 grams of silica ( $\text{SiO}_2$ ) and 600 grams of carbon. This charge was heated in a graphite crucible, as described in connection with Example 1, and afterwards subjected to acid leaching and gravity separation. The heavy portion recovered amounted to 1380 grams and consisted of tungsten monocarbide (WC), having a carbon content of 6.17%. Of the tungsten contained in the charge, 64.6% was recovered as tungsten monocarbide. Cobalt may be used instead of nickel in the charge.

#### Example 4

A charge was made up consisting of 1200 grams of scheelite (containing 75.19%  $\text{WO}_3$ ), 300 grams of iron in the form of steel chips, 150 grams of silica ( $\text{SiO}_2$ ) and 180 grams of carbon. This charge was placed in a graphite crucible and heated, in the manner described with reference to Example 1. After cooling, the regulus material was broken up and subjected to acid leaching and gravity separation, in the same way as in Example 1. The heavy portion recovered consisted of 480 grams of tungsten monocarbide (WC), having a carbon content of 6.17%. Of the tungsten contained in the charge, 62.8% was recovered as tungsten monocarbide.

#### Example 5

A charge was made up consisting of 1840 grams

of tungsten scrap, 600 grams of silica ( $\text{SiO}_2$ ), 1600 grams of nickel, and 200 grams of carbon. Cobalt may take the place of the nickel. This charge was placed in a graphite crucible and heated, to the temperatures and for the times described in Example 1. Thereafter, the regulus material was cooled, broken up and, then, subjected to acid leaching and gravity separation, as described in connection with Example 1. The heavy portion resulting consisted of 1200 grams of tungsten monocarbide (WC), having a carbon content of 6.12%. Of the tungsten contained in the charge, 61.3% was recovered in the tungsten monocarbide.

#### Example 6

A charge was prepared consisting of 1840 grams of tungsten scrap, 400 grams of silica ( $\text{SiO}_2$ ), 1000 grams of nickel, 300 grams of manganese dioxide ( $\text{MnO}_2$ ) and 300 grams of carbon. Instead of nickel, cobalt may be used. This charge was heated in a graphite crucible, as described in connection with Example 1, and, thereafter, the regulus material was cooled, broken up and subjected to acid leaching and gravity separation, as described in connection with Example 1. The heavy portion separated consisted of 1485 grams of tungsten monocarbide (WC), having a carbon content of 6.1%. Of the tungsten present in the charge, 75.8% was recovered in the tungsten monocarbide.

I am unable to state definitely the theory upon which this process operates, because the reactions taking place in the molten mass are complicated. However, I believe that the process, in general, works because the carbon prefers to unite with tungsten, to form tungsten monocarbide, rather than with other metals in the molten mass, and that, on the other hand, the silicon prefers to combine with the other metals to form silicides. The tungsten monocarbide is of considerably higher melting point than the other compounds formed, and it may be that it crystallizes, in the molten mass, at an earlier stage than any of the other compounds. However this may be, the fact is that the regulus material, when broken up and subjected to acid leaching, yields an acid-insoluble portion, which may be separated by gravity concentration methods into a light portion and a heavy portion. I believe that the light portion consists largely of silicides of metals, other than tungsten, contained in the molten mass, and I have found that the heavy portion consists entirely of tungsten monocarbide (WC). The compounds resulting from this process are such that those insoluble under the acid leaching treatment differ very noticeably in density, the tungsten monocarbide of the heavy portion having a density about three times that of the material in the light portion. Of course, the silicides of such metals as iron, manganese, nickel and cobalt, are about one-third the density of tungsten monocarbide (WC).

I am aware that the process herein described can be modified and changed in several particulars, without departing from the spirit of my invention, and, therefore, I claim my invention broadly, as indicated by the appended claims.

Having thus described my invention, what I claim as new and useful and desire to secure by Letters Patent, is:

1. The process of producing tungsten monocarbide (WC) from tungsten-containing material comprising the preparation of a charge containing the said material, silicon and carbon, heat-

ing the charge to a temperature above 2000° C. to cause carbon to combine with tungsten to form tungsten carbide and silicon to combine with other metals in the charge to form silicides thereby preventing the formation of insoluble inter-metallic compounds with tungsten, cooling the resulting regulus, leaching the regulus material with acid to remove the acid-soluble portion thereof, and subjecting the remaining undissolved portion to gravity separation to separate a light portion, relatively low in density, containing the silicides, from a heavy portion, relatively high in density, the heavy portion consisting substantially of tungsten monocarbide (WC).

2. The process of claim 1 in which the silicon is added in the form of silica ( $\text{SiO}_2$ ).

3. The process of claim 2 in which the silica of the charge constitutes at least 4% of the weight of the tungsten-containing material.

4. The process of claim 3 in which the carbon of the charge constitutes at least 10% of the weight of the tungsten-containing material.

5. The process of claim 4 in which the charge is heated in a carbon crucible.

6. The process of claim 5 in which the charge is maintained at a temperature of about 2500° C. for about three hours.

7. The process of claim 6 in which the light portion has a density no more than half that of the heavy portion.

8. The process of producing tungsten monocarbide (WC) from tungsten-containing material comprising the preparation of a charge containing said material, silicon, carbon and a metal of the group consisting of iron, manganese, cobalt and nickel, heating the charge to a temperature above 2000° C. to cause the tungsten to combine with carbon to form tungsten carbide and the silicon to combine with the metal to form silicides thereby preventing the formation of intermetallic compounds with tungsten, cooling the resulting regulus, leaching the regulus material with acid to remove the acid-soluble portion thereof, and subjecting the remaining undissolved portion to gravity separation to separate a light portion, relatively low in density, containing the silicides, from a heavy portion, relatively high in density, the heavy portion consisting substantially of tungsten monocarbide (WC).

9. The process of claim 8 in which the silicon is added in the form of silica ( $\text{SiO}_2$ ).

10. The process of claim 9 in which the silica of the charge constitutes at least 4% of the weight of the tungsten-containing material.

11. The process of claim 10 in which the carbon of the charge constitutes at least 10% of the weight of the tungsten-containing material.

12. The process of claim 11 in which the charge is heated in a carbon crucible.

13. The process of claim 12 in which the charge is maintained at a temperature of about 2500° C. for about three hours.

14. The process of claim 13 in which the light portion has a density no more than half that of the heavy portion.

15. The process of producing tungsten monocarbide (WC) from tungsten-containing ore selected from the group consisting of wolframite, hubnerite and scheelite comprising the preparation of a charge containing said ore, silicon, iron and carbon, heating the charge to a temperature above 2000° C., cooling the resulting regulus, leaching the regulus material with acid to remove the acid-soluble portion thereof, and subjecting the remaining undissolved portion to

gravity separation to separate a light portion, relatively low in density, from a heavy portion, relatively high in density, the heavy portion consisting substantially of tungsten monocarbide (WC).

16. The process of producing tungsten monocarbide (WC) from the tungsten-containing ore known as wolframite comprising the preparation of a charge containing wolframite, silicon and carbon, heating the charge to a temperature above 2000° C., cooling the resulting regulus, leaching the regulus material with acid to remove the acid-soluble portion thereof, and subjecting the remaining undissolved portion to gravity separation to separate a light portion, relatively low in density, from a heavy portion, relatively high in density, the heavy portion consisting substantially of tungsten monocarbide (WC).

17. The process of claim 16 in which silicon is present in the charge as silica to the extent of at least 4% of the weight of the wolframite.

18. The process of claim 17 in which carbon is present in the charge to the extent of at least 10% of the weight of the wolframite.

19. The process of claim 18 in which the charge contains a substantial percentage of nickel.

20. The process of claim 19 in which the charge contains a substantial percentage of manganese-dioxide ( $\text{MnO}_2$ ).

21. The process of producing tungsten monocarbide (WC) from the tungsten-containing ore known as hubnerite comprising the preparation of a charge containing hubnerite, silicon, and carbon, heating the charge to a temperature above 2000° C., cooling the resulting regulus, leaching the regulus material with acid to remove the acid-soluble portion thereof, and subjecting the remaining undissolved portion to gravity separation to separate a light portion, relatively low in density, from a heavy portion, relatively high in density, the heavy portion consisting substantially of tungsten monocarbide (WC).

22. The process of claim 21 in which the silicon is present in the charge as silica ( $\text{SiO}_2$ ) to the extent of at least 4% of the weight of the hubnerite.

23. The process of claim 22 in which the carbon in the charge amounts to at least 10% of the weight of the hubnerite.

24. The process of claim 23 in which the charge contains a substantial amount of nickel.

25. The process of producing tungsten monocarbide (WC) from the tungsten-containing ore known as scheelite comprising the preparation of a charge containing scheelite, silicon, carbon and a metal of the group consisting of iron, manganese, cobalt and nickel, heating the charge to a temperature above 2000° C., cooling the resulting regulus, leaching the regulus material with acid to remove the acid-soluble portion thereof, and subjecting the remaining undissolved portion to gravity separation to separate a light portion, relatively low in density, from a heavy portion, relatively high in density, the heavy portion consisting substantially of tungsten monocarbide (WC).

26. The process of claim 25 in which the charge contains silicon in the form of silica ( $\text{SiO}_2$ ) to the extent of at least 5% of the weight of the scheelite.

27. The process of claim 26 in which the charge contains carbon to the extent of at least 10% of the weight of the scheelite.

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28. The process of claim 27 in which the metal contained in the charge is iron to the extent of about 25% of the weight of the scheelite.

29. The process of producing tungsten monocarbide (WC) from the tungsten-containing ore known as scheelite comprising the preparation of a charge containing, by weight, about 66% scheelite, 8% silica ( $\text{SiO}_2$ ), 16% iron and 10% carbon, heating the charge to a temperature above  $2000^\circ\text{C}$ ., cooling the resulting regulus, leaching the regulus material with acid to remove the acid-soluble portion thereof, and subjecting the remaining undissolved portion to gravity separation to separate a light portion, relatively low in density, from a heavy portion, relatively high in density, the heavy portion consisting substantially of tungsten monocarbide (WC).

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