Candidate's Answer Paper

The present invention relates to further uses of metal oxycarbides, particularly of vanadium oxyca (VOC), in the technical field of metals and alloys.

Metal oxycarbides such as VOC are known to be useful in the field of metals and alloys. Document I teaches that VOC can be used to prepare carbides and/or nitrides which can be added to molten steel. Document II teaches that various compounds, including metal oxycarbides, can be used for coating hardmetal cutting tools. Document II teaches that the oxycarbides can be formed in situ by chemical vapour deposition onto the surface of a metal tool. There are as yet no known methods of using metal oxycarbides directly in the improvement and production of alloys and in the preparation of elementary metals.

The problem solved by the present invention is therefore to provide further processes for the improvement and production of alloys and the preparation of elementary metals, which processes involve the direct use of metal oxycarbides. It has surprisingly been found that such process are possible if the metal oxycarbides are used in the absence of oxygen.

Accordingly, the present invention provides, as a first aspect < claim 1 >.

The vanadium oxycarbide can be produced by the methods described in **Document I**. Basically, an oxidic material containing **V** is reacted with a gaseous hydrocarbon, such as natural gas - preferably containing a high proportion of methane - or methane itself, at temperatures of from 800 to 1,250°C. The reaction is preferably carried out in a fluidised bed, as described in Document I, as this optimises contact between the reactants and offers especially favourable conditions for controlling the temperature of the reaction mixture.

The addition of the **VOC** to the molten steel is quite simple, and can be done as in the known processes, using nitrides, carbides or ferrovanadium. To minimise oxidation losses, the vanadium is generally added in the absence of oxygen, preferably as late as possible, e.g. just before pouring. The steel obtained will, in general, contain from 0.1% to 0.5% **V**, as usual.

The use of vanadium oxycarbide as defined in claim 15 as an additive in steel making in the absence of oxygen is novel and inventive and also forms part of the invention.

~~The starting material consists mainly of vanadium oxycarbide, but may contain other components, e.g. free carbon.~~ As used herein "Vanadium oxycarbide" refers to compounds which are generally known by the formula **VOC**. However, they would be better described by the formula VO_xC_y, where the ratio of **x** to **y** may have any ratio to one another, although both must be greater than zero. Preferably, $x \geq y$. ~~The starting material is made, for example, by adding a material that contains vanadium in some oxidic form to a certain amount of carbon and heating the mixture. Alternatively the starting material may be prepared at high temperatures by reacting a material containing oxidised vanadium - as described above - with a gas that contains at least one hydrocarbon (preferably methane, though natural gas has also proved suitable).~~

Other metal oxycarbides can be defined in an analogous manner.

In a second aspect, the invention provides < claim 3>. The VOC can be contacted with molten iron, aluminium, nickel and/or manganese is any fashion. Thus, <claim 4>.

~~Ferrovanadium is produced in a similar way, by adding~~ When ferrovanadium is produced, **VOC** can be added to molten iron in the absence of oxygen. Alternatively, the VOC can be compressed with iron, in powder form, into a tablet which is then heated, again in the absence of oxygen, until the mixture melts. As usual, the ferrovanadium alloys will rarely contain less than 30% vanadium, and generally contain 50-80%. The other alloys mentioned above can be produced by the same method.

Where the VOC is contacted with iron to produce ferrovanadium, the process may further c use of the ferrovanadium to introduce vanadium into molten steel. Such introduction may b in the same way in which conventional ferrovanadium prepared by reduction of vanadium com with ferrosilicon has been used for the purpose. Thus, the present invention also provides <clai

Any steel into which vanadium has been introduced according to the invention may be subjected to conventional casting and rolling processing. Thus, also provided is <claim 7>.

~~Finally, the process described in point 3~~ The vanadium/manganese alloy obtained by the process of the invention can be used to produce very pure vanadium. This is done by adding **VOC** to molten **Mn** to form an alloy which is then freed of any slag and heated in vacuo to remove the manganese by volatilisation. The residue is vanadium of a higher purity than that obtained by the alternate method ~~described in point 4.~~ for the production of vanadium described below.

It has also been surprisingly found that metals of Groups 4 and 5 (Ti, Zr, Hf, V, Nb & Ta) can be prepared by heating a corresponding metal carboxide. Accordingly, the present invention provides, in a further aspect < claim 9>.

~~We wish to point out that~~ All the ~~above-mentioned~~ oxycarbides ~~investigated by us~~ have been known for many years. Like many carbides and nitrides, they belong to the class of so-called non-stoichiometric compounds.

To produce the ~~pure~~ metals ~~of transition Groups 4 and 5, it is necessary first to prepare the~~ oxycarbides, oxides of the metals ~~are~~ can be heated in a manner analogous to that described above with respect to vanadium, in the presence of a gaseous hydrocarbon such as natural gas or methane, to a temperature of at least 800°C. In the case of **Nb** and **Ta** oxycarbides, good yields can only be achieved using methane, at temperatures of 1,000-1,200°C.

To obtain the metal, the oxycarbide is then heated to a temperature of at least 1,600°C in the absence of oxygen, preferably in vacuo. The required minimum temperature depends on the metal. High yield and quality may require temperatures of 1,800°C or even 2,000°C. With plasma heating, temperatures up to 10,000°C have been used in the preparation of **Nb** and **Ti**. The oxycarbide decomposes to the metal, carbon and oxygen. The oxygen and carbon liberated react to form carbon monoxide. The metal is kept in the absence of oxygen until it has cooled down.

Preferred aspects of this process are set out in claims 10 to 14.

The expression "in the absence of oxygen" means that, for example, an inert layer of slag is placed over the melt so as to float on it and cover it completely. Alternatively, the operation may be carried under an inert atmosphere or in vacuo. For mass-production purposes, the steel, iron and aluminium industry tends to favour the slag method, but the other more valuable alloys and metals are generally prepared under an inert atmosphere or in vacuo. In contrast to slag, an inert atmosphere facilitates the escape of gaseous substances. A vacuum (eg. up to less than 10 Pa) has the further advantage of not requiring excessively high temperatures in decomposition reactions which lead to the release of volatile or gaseous substances.

The following examples illustrate the invention.

Unless otherwise stated, all quantities and percentages in the examples below refer to mass (weight). All the experiments were carried out in the absence of oxygen. This characteristic is essential for all embodiments of the invention.

CLAIMS

1) A process for the introduction of vanadium into steel, characterised in that vanadium oxycarbide is added directly to molten steel in the absence of oxygen.

2) A process according to claim 1, wherein the vanadium oxycarbide is added just before pouring of the molten steel.

3) A process for preparing an alloy of vanadium with iron, aluminium, nickel and/or manganese, characterised in that vanadium oxycarbide (VOC) is contacted with a melt of iron, aluminium, nickel and/or managanese in the absence of oxygen.

4) A process according to claim 3, wherein the VOC is added to molton iron, aluminium, nickel and/or manganese in the absence of oxygen or the VOC is added, in the absence of oxygen, to the required metal or metals and the thus obtained mixture is melted.

5) A process according to claim 3 or 4 wherein the VOC is contacted with iron to produce ferrovanadium.

6) A process for the introduction of vanadium into steel which process comprises preparing ferrovanadium by a process according to claim 5 and adding the thus obtained ferrovanadium to molten steel.

7) A process according to claim 2 or 6, further comprising casting and cooling the molton steel to prepare steel bars, and optionally rolling the steel bars to prepare steel sheets.

8) A process for the production of vanadium, which process comprises preparing a vanadium-manganese alloy by contacting VOC and manganese as specified in claim 3 or 4, removing any slag from the thus obtained alloy and heating the alloy in vacuo to eliminate manganese by volatilisation.

9) A process for preparing Ti, Zr, Hf, V, Nb or Ta in elementary form, characterised in that a corresponding metal oxycarbide is heated, in the absence of oxygen, to a temperature of at least 1,600°C.

10) A process according claim 9, wherein vanadium is prepared by heating VOC.

11) A process according to claim 9, wherein Ti, Zr or Hf is produced and wherein the corresponding metal oxycarbide is prepared by heating an oxidic material containing the metal with a gaseous hydrocarbon at from 800°C to 1250°C.

12) A process according to claim 9, wherein Nb or Ta is produced and wherein the corresponding metal oxycarbide is prepared by heating an oxidic material containing the metal with methane at from 1,000 to 1,200°C.

13) A process according to any one of claims 9 to 12, wherein the metal oxycarbide is heated in vacuo.

14) A process according to any one of claims 9 to 13, wherein the metal oxycarbide is heated at at least 1,800°C.

15) Use of vanadium oxycarbide of formula VO_xC_y wherein $x \geq y$, in the absence of oxygen, as an additive in steel making.

Note to Examiner

Unity

The following claims define separate inventions:

Claims 1 & 2 (& claim 7 insofar as is it refers to claim 2)
claims 3 - 6 (" " " " " " " " " " 6)
" 8
claims 9 -14; and
claim 15

However, all inventions are linked by a special technical feature. That is the requirement that the metal carboxide be handled in the absence of oxygen. This feature defines contribution which each of inventions makes over prior art & therefore suffices to link features (Rule 30 EPC). The requirements of Art 82 EPC are ∴ satisfied.

Referring to claims

Claims 1 & 2:

Product by process claim not included. Client notes that pure metals (including steel) already known (98/A(C)/e/2 last para). Product-by-process claims only allowable if product = novel & inventive per se (T150/82).

Claims 3 & 4

Client gives 2 ways of preparing alloys - adding VOC to molten metal & adding VOC to powdered metals & then melting. Clearly, what is important is that VOC comes into contact with molten metal. Claim 3 is ∴ broadly worded, claim 4 covers client's method exactly.

Claim 7

Added to optimise product-by-process protection which Art 64(2) EPC confers on "direct products" of patented processes.

Claim 9

All oxycarbides well known (p. 4. penultinate para). Starting materials for this process are ∴ available.

Claim 15

Client notes that use of VOC in steel making novel (p. 2 lines 4-5). However, DI defines VOC as VO_xC_y where x & y can have any ratio to each other. Client's letter refers to DI for preparation of VOC.

Example I of DI discloses a compound falling within general definition given for use in steel making. However, O_2 content v. low (0.8%). Claim 15 ∴ claims use of VOC wherein O_2 content at least as high as C content. Thus should be novel & inventive over DI.