

EUROPEAN QUALIFYING EXAMINATION 1998

PAPER A CHEMISTRY

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CLIENT'S LETTER

Dear Sir/Madam,

We have received information that our competitors are working in the area of the invention described below. They are clearly at the point of completing their research, as they have told customers that new products will shortly be available for testing. We would therefore ask you to file a patent application on our behalf, preferably before the end of this week.

Our main business is in metals, alloys and additives for use in the steel industry. We have taken the precaution of enclosing two documents which will give you some more information about the field in question and will presumably also need to be considered in drafting the patent application.

The additives referred to contain, in one form or another, metals which form alloys with iron (Fe). They are added to molten iron during the steel-making process so that various properties of the steel product are improved.

Recently, in the course of these experiments a simple way of adding vanadium to steel has been sought. This element (V) is known to have an effect on grain refinement and hardenability of steel.

Two main ways of introducing V into steel are known in the art. In one, vanadium can be added in the form of carbide and/or nitride directly into the molten steel. As indicated in our patent application of three years ago (**Document I**), the compounds suitable for this purpose are produced from vanadium oxycarbides (VOC). In the second way, vanadium can be added to the molten steel in the form of a vanadium-rich iron alloy. Up to now, these so-called ferrovanadium alloys have been made in various ways, for example by reduction of vanadium compounds with ferrosilicon.

There is still a need however to devise new ways by which vanadium can be added to steel.

In the course of our experiments we have made several observations, briefly summarised below, which we would like to patent as far as possible. The summary of our findings is followed by a more detailed

description of the process conditions.

1. We have found that, in contrast to the teaching of **Document I**, the **VOC** does not in fact have to be converted to the carbide or nitride before addition to the molten steel. Instead, **VOC** can be added directly to the molten steel in the absence of oxygen. We did not know this at the time of filing **Document I**. The process is thus simplified. **VOC** itself has apparently not been used before in steel-making. Compared with the use of vanadium carbide or carbide/ nitride mixes, **VOC** has the additional advantage that less carbon is incorporated into the steel. This can be important for some steel applications.
2. It has become apparent that **VOC** is also an excellent starting material for the production of ferrovanadium, which provides an alternative means of adding vanadium to steel.
3. Alloys of **V** with aluminium (**Al**), nickel (**Ni**) and/or manganese (**Mn**) can also be produced in this way. For this purpose, the **VOC** is added to a melt of one or more of the other metals in the absence of oxygen.
4. We have also found that vanadium of high purity can be produced by heating **VOC** in the absence of oxygen.
5. This phenomenon (production of pure metal) is not limited to vanadium but occurs with all the transition group metals of Groups IVb and Vb (or, under the new IUPAC nomenclature, Groups 4 and 5), i.e. titanium (**Ti**), zirconium (**Zr**), hafnium (**Hf**), vanadium (**V**), niobium (**Nb**) and tantalum (**Ta**). For these elements, the metal oxycarbide is produced by reacting an oxygen-containing compound of the metal with a hydrocarbon-containing gas. The oxycarbide thus obtained is then heated, in the absence of oxygen, to a temperature which depends on the metal used but is in each case at least 1,600°C. The process provides a new method for preparing these metals in elementary form.

It should be noted that all these metals have already been prepared in varying degrees of purity (sometimes in an extremely pure form) by other processes. Reference is made, for example, to the *Van Arkel - de Boer* process, known from textbooks in the field.

6. Finally, the process described in point 3 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 method described in point 4.

The 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 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.

Ferrovanadium is produced in a similar way, by adding **VOC** 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.

Vanadium metal is prepared by simply heating the **VOC**, in vacuo or under an inert atmosphere, to at least 1,600°C.

To produce the pure metals of transition Groups 4 and 5, it is necessary first to prepare the oxycarbides. Oxides of the metals are 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 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.

VOC can be used with **Al**, **Ni** and/or **Mn** to prepare alloys of **V** with one or more of these metals. A desired amount of **VOC** is added, in the absence of oxygen, to the required metal or metals, and the mixture is melted. Alternatively, the other metal may be in a molten state before the **VOC** is added.

Especially pure vanadium may be obtained by adding **VOC** to molten **Mn** to form an alloy which is then heated in vacuo to decompose it and eliminate the **Mn** by volatilisation.

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.

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.

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.

Example 1

Purified natural gas was passed over vanadium pentoxide V_2O_5 at $1,000^\circ C$. The product **VOC**, containing 14% oxygen and 10.5% carbon, was heated to a temperature of $1,650^\circ C$ in vacuo in a furnace for 5 hours. The final pressure was 1.3 mPa. After cooling, the vanadium metal contained less than 0.15% oxygen and less than 0.15% carbon.

Example 2

VOC was obtained by passing natural gas over technical-grade V_2O_5 at a temperature from about 800 to $1,250^\circ C$. The **VOC** contained 67.4% V, 19.7% oxygen and 10.3% carbon. The oxycarbide was then added to molten steel containing 0.04% oxygen and 0.06% carbon, in a weight ratio of 1:195 at a temperature of approximately $1,650^\circ C$. After cooling, the steel contained 0.34% vanadium, 0.04% oxygen and 0.01% carbon. The vanadium yield therefore amounted to 98%.

Example 3

26.0 parts of **VOC**, containing 75.7% vanadium, 9.1% oxygen and 12.5% carbon, and prepared by passing natural gas over V_2O_5 , were added to 58.8 parts of molten aluminium. The melt was then heated to $1,670^\circ C$. After cooling, an aluminium vanadium alloy was obtained consisting of 75.8% Al, 21.0% V, 1.5% O and 1.7% C.

Example 4

3.64 grams of niobium oxycarbide containing 10% O and 7.5% C were heated in vacuo in a furnace for 4 hours at $1,700^\circ C$. The final pressure was 13.3 mPa. The resulting powdery niobium contained 1.2% O and 0.3% C after cooling.

We would like you to include, if possible, all aspects of our research in the patent application, and we look forward to receiving official confirmation of filing.

Yours sincerely,

I.M. Ironman

DOCUMENT I (State of the Art)

The invention relates to a method of preparing vanadium carbide and/or nitride. These compounds are used as additives in the production of steel alloys containing vanadium.

The subject-matter of the invention is a method of preparing a material containing vanadium compounds
5 having the general formula VC_cN_n , wherein, within the range of possible oxidation states for vanadium, c and n may have any ratio to one another and either c or n may equal zero, but not both simultaneously. The method involves heating vanadium oxycarbide for an extended period at a high temperature with a gas containing one or more of hydrogen (H_2), ammonia (NH_3) and nitrogen (N_2). Such compounds are often referred to as non-stoichiometric, because, within certain limits, their composition can be varied almost
10 infinitely by modifying the reaction conditions and the make-up of the reaction mixture, and their composition can only be given approximately. This applies to many carbides, nitrides and oxides of transition metals and their mixed compounds.

The starting material consists mainly of vanadium oxycarbide, but may contain other components, e.g. free
15 carbon. "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
20 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).

The formula VC_cN_n refers to vanadium carbide, vanadium nitride, or mixtures of the two. The range of products covered by this definition depends on the exact composition of the gases used in the conversion,
25 the composition of the VOC , and the specific reaction conditions. The purity of the reactants is an

important aspect. For example, the VOC can be very pure or it may still contain some carbon in some form, depending on the method of preparation.

5 The conversion of the VOC to VC_cN_n is generally carried out at a temperature of from 800 to 1,250°C in a closed reactor providing for good mixing of the reactants. A fluidised bed is for example suitable for this purpose.

The products with the formula VC_cN_n according to the invention may be added to molten steel in the ladle or in the mould.

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The quoted percentages refer to weight (mass).

Example 1

7 litres of natural gas were passed over 10 grams of technical-grade vanadium pentoxide for one hour at 15 1,150°C. A further 4 litres of gas were then passed over the material at the same temperature and for the same length of time. The reacted material contained 72.7% vanadium, 16.9% carbon and 10.5% oxygen. Hydrogen was then passed over this material for 7 hours at the rate of 20 litres per hour and at a temperature of 1,250°C. The resulting carbide contained 82.6% V, 14.9% C and 0.8% O. This vanadium carbide is an excellent additive for use in steelmaking.

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Example 2

Example 1 was modified by replacing the pure hydrogen with a 1:1 mixture of hydrogen and nitrogen. The product contained 81.3% vanadium, 8.5% nitrogen, 8.5% carbon and 0.5% oxygen. This material is also an excellent additive for use in steelmaking.

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Patent claims

1. A method for the preparation of a material containing vanadium compounds having the general formula VC_cN_n , where c and n may have any ratio to one another and either c or n may equal zero, but not both simultaneously, comprising the heating of vanadium oxycarbide for an extended period at a high 30 temperature with a gas containing one or more of hydrogen, ammonia and nitrogen.
2. Method according to claim 1, characterised in that the reaction is carried out at a temperature of from 800 to 1,250°C.

Document II (State of the Art)

Our investigations described below have been concerned with the use of carbides, oxycarbonitrides, oxycarbides of transition metals belonging to Groups 4 to 6 in the periodic system of elements, especially titanium (**Ti**), zirconium (**Zr**), vanadium (**V**), niobium (**Nb**) and tungsten (**W**), as well as aluminium (**Al**) and boron (**B**), for coating hardmetal cutting tools. Tools of this kind are used for working metals at various
5 temperatures. They are often exposed to considerable mechanical and thermal stress. The aim of our investigations was to find materials which had improved properties in this respect.

The carbides, oxycarbides and oxycarbonitrides are produced in situ on the surface of the metal when gas mixtures containing, for example, the metal chloride and mixtures of H_2 and CO_2 and/or CH_4 , and possibly
10 N_2 , are used in the gas phase precipitation (chemical vapour deposition: **CVD**) of the metal onto the surface of the metal tool. The precise composition of the gas mixture will of course depend on the desired composition of the surface coating. **CVD** is often carried out in such a way as to form a protective coating against wear, containing at least one of the compounds mentioned, with a thickness of about 0.1 to 2 μm .

15 These coatings adhere firmly to the surface of the tool and offer good resistance to fracture and wear. They increase the mechanical strength and resistance of the tool. Usually, several layers of varying composition are applied by changing the composition of the gas and the temperature at which the **CVD** process is carried out.

20 **Example**

A clean cutting tool of hard metal was coated at 1,020°C for 10 minutes using the **CVD** process with the gas composition listed below as **A1**. The temperature was then raised to 1,050° C for 40 minutes, using gas mixture **A2** and adding short blasts of nitrogen at regular intervals. In a third step, mixture **A3** was used

for about 5 minutes, adding A4 for a short time. A4 was then used for 20 minutes. Finally, A1 was used over the tool again for 20 minutes:

5	A1	TiCl ₄	4 vol%
		N ₂	40 vol%
		H ₂	56 vol%
10	A2	TiCl ₄	3.5 vol%
		CH ₄	9 vol%
		H ₂	Remainder to 100%
15	A3	TiCl ₄	4.5 vol%
		CH ₄	2 vol%
		N ₂	18 vol%
		CO ₂	0.1 vol%
		H ₂	Remainder to 100%
20	A4	AlCl ₃	2.5 vol%
		CO ₂	4.5 vol%
		H ₂	40 vol%
		N ₂	Remainder to 100%

The coating consisted of the following sequence of layers: titanium nitride, titanium carbide, titanium oxycarbide containing nitrogen, carbon, oxygen and aluminium, aluminium oxide containing nitrogen and carbon, and finally titanium nitride again.