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D E C I S I O N
of 15 November 1998

Case Number: T 0754/96 - 3.2.2

Application Number: 92306354.9

Publication Number: 0522873

IPC: C23C 30/00

Language of the proceedings: EN

Title of invention:
Non-stoichiometric titanium nitride coating

Applicant:
Praxair S.T. Technology, Inc.

Opponent:
-

Headword:
-

Relevant legal provisions:
EPC Art. 54

Keyword:
"Novelty (yes, after amendments)"
"Remittal to the first instance"

Decisions cited:
-

Catchword:
-

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Case Number: T 0754/96 - 3.2.2

D E C I S I O N
of the Technical Board of Appeal 3.2.2
of 15 November 1998

Appellant: Praxair S.T. Technology, Inc.
441 Sackett Point Road
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Representative: W.P. Thompson & Co.
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Church Street
Liverpool L1 3AB (GB)

Decision under appeal: Decision of the Examining Division of the European Patent Office posted 1 April 1996 refusing European patent application No. 92 306 354.9 pursuant to Article 97(1) EPC.

Composition of the Board:

Chairman: W. D. Weiß
Members: R. Ries
J. C. M. De Preter

Summary of Facts and Submissions

I. European patent application No. 92 306 354.9 (publication No. 0 522 873) was refused on 1 April 1996 by decision of the Examining Division for the reason that the subject matter of claims 1 to 6 and 8, 9 was not novel having regard to the prior art document

D1: EP-A-0 418 001.

The subject matter of dependent claim 7 was held to lack an inventive step.

II. The appellant (applicant) lodged an appeal on 30 May 1996 against the decision of the first instance. A statement of grounds was submitted on 1 August 1996.

III. Enclosed with its letter of 2 October 1998 in response to the official communication of 3 June 1998, the appellant submitted a revised set of claims 1 to 8 to be substituted for all earlier requests.

Independent product claim 1 reads as follows:

"1. A coated article comprising a substrate having a pure titanium outer surface or a substrate having a coating of pure titanium, on which a non-stoichiometric, titanium nitride coating having good wear and corrosion resistance, is deposited, the coating having a crystallite size, measured in the direction perpendicular to the (111) diffraction plane, of less than 55 nm, and containing from 32.5 to 47 atomic percent nitrogen."

IV. The appellant requests that the decision under appeal be set aside and that a patent be granted on the basis of revised claims 1 to 8 submitted on 2 October 1998.

V. The appellant's arguments are as follows:

- The present invention pertains to a substrate on which a non-stoichiometric TiN_{1-x} coating is deposited. This coating provides an excellent match of good wear resistance and/or erosion characteristics to solid particles. An improved bonding between the titanium nitride coating and the substrate is achieved due to an titanium outer surface of the substrate.

- Document D1 is primarily directed to multi-layer coatings, with the single layer coatings of samples 6 and 7 being merely comparative test results of no consequence. Contrary to the teaching of document D1, the present application provides a titanium substrate or a substrate having a titanium outer surface rather than the non-nitrogen **titanium containing surface** as set out in document D1. The titanium surface is important to the formation of a fine grain structure of the coating and to the improved bonding of the titanium nitride coating to the substrate. Thereby, the performance characteristics of the coated article are enhanced.

- Hence the claimed coated article is clearly distinguished from the subject matter of the prior art represented by D1 and therefore novel.

Reasons for the Decision

1. The appeal is admissible.

2. *Amendments*

With respect to the claims underlying the appealed decision, the subject matter of claim 1 has been amended so as to be more precisely distinguished from the disclosure of the closest prior art document D1, however, without adding new subject matter.

To this end, present claim 1 clearly defines that the substrate to be coated has a **pure** titanium outer surface or, alternatively, has a coating of **pure** titanium on which a non-stoichiometric titanium nitride coating is deposited. This amendment finds support on page 6 last paragraph bridging page 7, 2nd full paragraph of the specification as originally filed, showing that the substrate preferably consists of titanium or titanium coated Fe, Al, Ni, Co. It is unambiguously and clearly deducible from the whole context of the application read in combination with the physical vapour deposition process described in the examples that the term "titanium" should mean "pure titanium" rather than a titanium alloy. Specifically, before depositing the TiN_{1-x} layer, Ti is evaporated from a Ti cathode to provide a deposit of about 1 micron of Ti on a Ti-6Al-4V substrate. It is further evident that the present application is not concerned with multi-layer coatings of non-stoichiometric TiN_{1-x} as is D1, but rather more with a single layer TiN_{1-x} coating, as is reflected by the wording "a substrate, on which **a** non-stoichiometric titanium nitride **coating** is deposited" in present claim 1.

The crystallite size and the atomic percent of nitrogen of the titanium nitride coating defined in amended claim 1 have a basis on page 4, the last two lines bridging page 5, line 2 of the originally filed application.

The dependent claims 2 to 8 correspond to claims 2 to 8 as originally filed.

It results from the above that the amendments to claim 1 meet all the requirements of Articles 84 and 123(2) EPC.

3. *Novelty*

3.1 Document D1 is concerned with a multi-layer coated substrate comprising at least two layers of a nitride containing compound wherein the composition of each layer contains at least 2 atomic percent of nitrogen different from the nitrogen contained in the adjacent layer (cf. D1, claim 1). In a more preferred embodiment according to claim 3 of D1, the nitrogen containing compound of one layer comprises 33 to 45 at% nitrogen and the adjacent layer has a nitrogen content from 40 to 55 at%. The multi-layer coated substrate is selected from titanium, steel, aluminium, nickel, cobalt or alloys thereof (cf. claim 10). For comparison with samples 1 to 5 which all relate to multi-layer coatings having a total number of layers in the range of 18 to 38, Table 2 of document D1 further discloses one substoichiometric TiN_{1-x} **single** layer coating, (Table 2, comparative sample 7), comprising 41 at% N_2 and a crystallite size, which was determined based on the (111) diffraction lines broadening, of 20.6 nm (cf. Table 3). In Example 1 of D1, the multi-layer coatings and the single layer coating were deposited on a Ti-6Al-4V substrate (cf. page 5, lines 4, 26, 27) and

in Example 2, multi- and single layer coatings were deposited on a substrate consisting of INCONEL, i.e. a nickel based alloy consisting of 76% Ni, 15% Cr and 9% Fe (cf. D1, page 7, lines 7 to 11).

3.2 With respect to the teaching of document D1, the subject matter of present claim 1 is distinguished by the following features:

- the substrate is coated with a (single) non-stoichiometric coating rather than a multi-layered coating;

- the substrate exhibits an outer surface of pure titanium or, alternatively, a coating of pure titanium.

Although according to claim 10 of D1 the substrate can be selected from (pure) titanium, this is disclosed only in combination with a multi-layer coating on the substrate and there is no description of a particular example in D1, showing a multi-layer coated substrate consisting of (pure) titanium. The specific embodiment of D1 given in Example 1 discloses a Ti-6Al-4V substrate, i.e. **a titanium alloy**, on which all single and multi layer TiN_{1-x} coatings are deposited. It can be noted from example 1 of the present application that the same Ti-6Al-4V alloy substrate is used (cf. Example 1, page 7, last paragraph bridging page 8 paragraph 1). After sputtering to remove surface contaminants, Ti is evaporated in an argon environment so as to deposit about 1 micron of titanium on the substrate and **then** the argon is changed to an argon-nitrogen reactive gas mixture to form the singular TiN_{1-x} coating. The technical reasons for selecting the pure titanium outer surface or the pure titanium coating on the substrate are given on page 7, lines 14 to 19 of the specification: titanium will effectively provide a

better adherence for the coating on the substrate. Contrary to the present application, the Ti-6Al-4V substrate in D1 is not coated with a layer of pure Ti before depositing the TiN_{1-x} single layer (or multi-layer) coating, as is required by present claim 1 and as is specifically disclosed in example 1 of the present application. It is also apparent from the method in D1, page 3, lines 12 to 39 for producing the multi-layer nitride coatings, that such an intermediate layer of pure Ti between the outer surface of the substrate and the multi-layer coating has not been envisaged.

Therefore, the subject matter of claim 1 is novel with respect to the technical teaching of document D1.

3.3 During the substantive examination, three further documents

D2: Thin Solid Films, vol. 158, no. 2, 1988, Lausanne, CH, pages 225 to 232

D3: Thin Solid Films, vol. 156, no. 1, 1988, Lausanne, CH, pages 53 to 63

D4: Thin Solid Films, vol. 107, no. 2, 1983, Lausanne, CH, pages 149 to 157

have been considered which are also mentioned on page 1 of the appealed decision.

Document D2 relates to the microhardness of the non-stoichiometric TiN layer. The substrate is made of 12%Cr-steel (see 2. Experimental Details). The same substrate has been used in document D3 which also

discloses in Figure 1 test results for microhardness, residual stress, etc of a substoichiometric titanium nitride layer. D4 uses a steel substrate for reactive sputtering of a single phase TiN layer comprising 47 at% N.

Thus, the subject matter of present claim 1 is novel also with respect to the technical teaching of documents D2 to D4.

4. Given that the reasons set out in the decision of the Examining Division for refusing the application no longer apply, the Board takes the view to set aside the decision under appeal. The first instance has not yet examined whether or not the present application as amended meets the requirements of inventive step. It is, therefore, considered as being appropriate, in accordance with Article 111(1) EPC and in order to avoid loss of an instance, to remit the case to the first instance for further prosecution.

5. It is also noted that, on page 5, paragraph 1 of the amended description submitted on 1 August 1996, the crystallite size of 50 nm does not comply with the crystallite size of 55 nm defined in claim 1 and appears to relate to a preferred embodiment.

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.

2. The case is remitted to the first instance for further prosecution on the basis of the following documents:

claims: 1 to 8 as submitted on 2 October 1998

description: page 4 as submitted on 2 October 1998
pages 1 to 3, 5 to 7 as submitted on 1 August 1998
pages 8 to 17 as originally filed

drawings: sheets 1/5 to 5/5 as originally filed.

The Registrar: The Chairman:

S. Fabiani W. D. Weiß