

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(10) International Publication Number  
**WO 2017/174197 A1**

(43) International Publication Date  
12 October 2017 (12.10.2017)

(51) International Patent Classification:

C23C 14/00 (2006.01) C23C 28/04 (2006.01)  
C23C 14/06 (2006.01) C23C 30/00 (2006.01)

(21) International Application Number:

PCT/EP2017/000437

(22) International Filing Date:

7 April 2017 (07.04.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

10 2016 003 998.1 7 April 2016 (07.04.2016) DE

(71) Applicant: OERLIKON SURFACE SOLUTIONS AG,  
PFÄFFIKON [CH/CH]; Churerstrasse 120, 8808 Pfäffikon (CH).

(72) Inventors: KARNER, Johann; Aeulestrasse 28, 9495 Triesen (LI). BEGANOVIC, Neir; Rietlistrasse 9, 9470 Buchs (CH). RAMM, Juergen; Mühlebündtestrasse 12, 7304 Maienfeld (CH). WIDRIG, Beno; Kirchgasse 4, 7310 Bad Ragaz (CH).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

— with international search report (Art. 21(3))



WO 2017/174197 A1

(54) Title: WEAR AND/OR FRICTION REDUCTION BY USING MOLYBDENUM NITRIDE BASED COATINGS

(57) Abstract: The present invention relates to a component comprising a surface coated with a coating comprising a MoxCryN layer, where x and y correspond to the coefficients of Mo content and Cr content in atomic percentage, respectively, when only Mp and Cr are considered, and so x+y is considered to be 100 at%.

**Wear and/or friction reduction by using molybdenum nitride based coatings**

The present invention relates to coatings for attaining reduction of wear or reduction of friction on surfaces of components. Such components for example can be used in the automotive sector or precision components (i.e. highly engineered components) sector. In this regard the components can be for example piston pins, cam followers or piston rings or nozzle needles.

The use of molybdenum coatings or molybdenum comprising coatings is well known. The use of molybdenum nitride as wear reduction coating on surfaces of components is in particular well known.

10 The behavior of the interface between the substrate surface of the component and the molybdenum nitride coating is however still today unsatisfactory and insufficient for meeting the current industrial requirements during application of the so coated components.

This has been especially observed when the substrate material to be coated is not hard enough, it means in this context that the substrate material has a hardness for example 15 between 50-65 HRC, in any case not higher than 65 HRC.

Figure 1 shows a picture of a coated surface after Rockwell indentation HRC, where the hardness of the substrate is between 50 and 65 HRC and the substrate is coated with MoN. Ring-shaped fracture of the MoN coating can be clearly observed surrounding the HRC Rockwell indentation.

20 It is possible that the observed ring-shaped fracture has been produced as a consequence of the big difference between the hardness and Young's modulus of the MoN coating and the hardness and Young's modulus of the substrate material. It is supposable, because actually the hardness and Young's modulus in the molybdenum nitride coating are considerable higher in comparison with the substrate, and consequently it is possible that the substrate has been 25 considerably deformed during the application of the indentation load, while the MoN coating has been less deformed ~~not~~ and therefore the MoN coating cracked.

For this reason this can be in particular a big problem when variable loads (interrupted load) are applied on the coated substrate of the component.

Essentially this problem can be avoided by using substrates having a higher hardness, such as e.g. substrates made of cemented carbide. However the components used in many automotive applications are made of materials which have Rockwell hardness lower than 65 HRC.

- 5 The objective of the present invention is to modify the molybdenum nitride coating and/or the substrate surface to be coated in order to improve the contact between substrate surface and MoN coating when the substrate exhibit a hardness of 65 HRC or lower and the coated substrate is subjected to load or especially to interrupted load.

10 In particular it is intended that the inventive solution makes possible that no ring-shaped fracture lines are produced during Rockwell indentation by conduction of HRC Rockwell tests in substrates coated with MoN based coatings when the substrate hardness is lower or equal to 65 HRC.

15 The objective of the present invention is attained by providing a component having a coated surface according to claim 1. Preferred embodiments of such components are described in claims 2 to 6.

Such components having a coated surface according to the present invention can be manufactured by using a method according to claim 7. A preferred method is described in claim 8.

20 According to a first possible solution the component surface to be coated with the MoN coating is previously modified by subjecting it to a nitriding process in order to increase the substrate surface hardness before depositing the MoN coating. Afterwards the MoN coating is applied on the component surface which was previously hardened by nitriding as mentioned above. The MoN coating can be deposited for example by using a reactive PVD process. Preferably a reactive arc PVD process is used for depositing the MoN coating on the hardened  
25 component surface. It is a special advantage of the used method that the nitriding process of the substrate and the coating process are done in one machine. This guarantees a good adhesion between the nitriding layer and the coating without formation of a white layer. The MoN coating can be deposited exhibiting a hexagonal phase or a cubic phase or a mixture of hexagonal and cubic phases.

Figure 2 shows a picture of a surface coated according to the above mentioned first possible solution and afterwards was tested according to the standard HRC Rockwell test. In this picture it is clear to see that no ring-shaped fracture lines surrounding the Rockwell indentation can be observed.

- 5 According to a second possible solution the component surface to be coated is coated with a modified MoN coating. In this case it is not necessary to modify previously the component surface to be coated. The modified MoN coating according to this second possible solution exhibits a multilayer structure, which comprises alternate deposited layers of MoN and layers of CrN. Especially good results i.e. Rockwell indentations without ring-shaped fracture lines or  
10 further adhesive failures were in particular observed by using this second possible solution when the thickness of the multilayer coating was about 4 to 5  $\mu\text{m}$ . Also in this case the MoN layers can be deposited exhibiting a hexagonal phase or a cubic phase or a mixture of hexagonal and cubic phases. It might be however that for a specific application less coating thickness is suitable because the load in a real application might be not as high as in the HRC  
15 Rockwell test. In this case a thickness of for example 2  $\mu\text{m}$  might be enough.

The MoN and CrN layers can be deposited for example by using a reactive PVD process. Preferably a reactive arc PVD process is used for depositing the MoN and the CrN layers.

- According to a preferred embodiment of the present invention the component surface to be coated is coated with a modified MoN coating, wherein the MoN coating is modified by  
20 adding Cr. In this case it is also not necessary to modify previously the component surface to be coated. The modified MoN coating according to this embodiment of the present invention is a Cr containing MoN coating exhibiting a monolayer structure and having chemical composition given by the formula  $\text{Mo}_x\text{Cr}_y\text{N}$ , where x and y correspond to the coefficients of Mo content and Cr content in atomic percentage, respectively, when only Mo and Cr are  
25 considered, and so  $x+y$  is considered to be 100 at%. Preferably  $5 \leq y \leq 50$ . More preferably  $20 \leq y \leq 40$ . The Cr content in the  $\text{Mo}_x\text{Cr}_y\text{N}$  can be varied along the thickness of the  $\text{Mo}_x\text{Cr}_y\text{N}$  layer.

- Since as described in the first possible solution the component surface to be coated with a MoN coating must be previously nitrided and standard nitriding processes are conducted at temperatures of 450 °C or higher, only components made of materials which can resist such  
30 temperatures can be treated in this manner. In this regard, the second possible solution (MoN/CrN multilayer) and the above mentioned preferred embodiment of the present

invention (MoxCryN) involves the advantage that the coating process can be conducted at temperatures of 200 °C and no nitriding step is necessary, hence components made of temperature sensitive materials can be treated, like for example piston pins.

Since the thickness of the individual layers of a multilayer coating comprising MoN and CrN layers as described in second possible solution can depend strongly on the geometry i.e. of the form and dimensions of the surface of the component to be treated as well as the position of the component surface to be coated in relation to the coating source during coating process. Consequently it could be complicated to produce such multilayer structures if the component to be treated has a complex geometry. In this regard, the preferred embodiment of the present invention involves the advantage that only a monolayer must be deposited. Furthermore this preferred embodiment involves the advantage that surprisingly with lower coating thicknesses of the MoxCryN layer, i.e. already with thickness of about 2 µm it was possible to obtain very good results and pictures of the treated surface after HRC Rockwell test. The HRC Rockwell test showed no ring-shaped fracture lines with 2 µm coating thickness and also not any sign of adhesive failure, while in the case of using a MoN/CrN multilayer a thickness of about 4 µm was necessary.

However as already mentioned above it might be, that in a real automotive application also a 2 µm thick MoN/CrN Multilayer solution would work.

It was observed that in some cases a further improved contact in the context of the present invention was attained by providing an adhesion layer made of CrN. This adhesion layer was deposited for example before depositing the MoN coating according to the first possible solution or before depositing the modified MoN coating according to the second possible solution, or before depositing the MoxCryN monolayer according to the above mentioned preferred embodiment of the present invention, respectively. The CrN adhesion layer is preferably provided having a layer thickness of at least 30 nm. The thickness of the CrN adhesion layer preferably between 0.05 µm and 1 µm.

#### **Examples:**

##### **Example 1**

A qualified reference sample made of 1.2842 19MnCrV8 with hardness 64 HRC before coating (following referred to as QRS) test piece having a steel surface and a piston pin were coated

with a coating comprising a first layer consisting of CrN, which was deposited as adhesion improving layer, and a MoxCryN monolayer according to the present invention was deposited onto the CrN layer. The CrN layer was deposited by evaporating two Cr targets by using Arc PVD techniques in a nitrogen containing atmosphere. MoxCryN layer was also deposited by means of a reactive Arc PVD process. For depositing the MoxCryN layer two targets comprising Mo and two targets comprising Mo were evaporated by using Arc PVD techniques in nitrogen comprising atmosphere. The desired element composition of the MoxCryN layer was adjusted by varying the arc current at the targets operated as cathodes. The element composition of the MoxCryN layer was measured by EDX and it was determined that y was approximately 34 at%. The thickness of the CrN and MoxCryN layer was also measured and it was determined that it was 0.4  $\mu\text{m}$  for the CrN layer and 2  $\mu\text{m}$  for the MoxCryN, respectively. No nitriding treatment was performed before coating.

With the intention of comparing the inventive coated surfaces with not inventive coated surfaces, a QRS and a piston pin were coated with a MoN coating (including a thin CrN adhesion layer) without performing previously a nitriding treatment.

Afterwards corresponding Rockwell tests were carried out on all coated surfaces.

The pictures of the tested surfaces after Rockwell indentation are shown in figure 3. Fig. 3a and 3b on the left side show the coated surface of the QRS (on the top) and the piston pin (on the bottom), respectively, which were only coated with a MoN coating. Fig. 3c and 3d on the right side show the coated surface of the QRS (on the top) and the piston pin (on the bottom), respectively, which were coated according to the above described example of the present invention.

Neither ring-shaped fracture lines nor any sign of adhesive failure were observed on the surfaces coated according to the present invention.

## Example 2

A nozzle needle was coated with a coating comprising a first layer consisting of CrN, which was deposited as adhesion improving layer, and a MoxCryN monolayer according to the present invention was deposited onto the CrN layer. The same method as described in example 1 was used for depositing the coating in this example. Only the arc current at the Cr targets was adjusted to be 20 Amperes higher during deposition of the MoxCryN monolayer in order to

obtain a higher Cr content in comparison with example 1. The thickness of the CrN and MoxCryN layer was measured and it was determined that it was 0.7  $\mu\text{m}$  for the CrN layer and 2.3  $\mu\text{m}$  for the MoxCryN, respectively.

5 Afterwards corresponding HRC Rockwell tests were carried out on the coated surface of the nozzle needle.

A picture of the tested surface after Rockwell indentation is shown in figure 4. Neither ring-shaped fracture lines nor any sign of adhesive failure were observed.

Particularly good results were observed with  $20 \leq \text{HRC} \leq 40$ .

10 The components coated according to the present invention can be produced by using any PVD technique. For example the MoxCryN layer can be deposited by means of a reactive PVD process. The reactive PVD process can be a reactive Arc PVD process, wherein during deposition of the MoxCryN at least one target comprising Mo and Cr or at least one target comprising Mo and at least one target comprising Cr are evaporated by using Arc PVD techniques in an atmosphere comprising nitrogen as reactive gas.

15 However the methods for producing coated components according to the present invention are not limited by this description.

The surfaces of the components coated according to the present invention exhibit additionally very good tribological properties, in particular concerning wear resistance and reduced friction.

20

**Claims**

1. Component comprising a surface coated with a coating comprising a MoxCryN layer, where x and y correspond to the coefficients of Mo content and Cr content in atomic percentage, respectively, when only Mo and Cr are considered, and so  $x+y = 100$  at%.
2. Component according to claim 1, characterized in that  $5 \text{ at\%} \leq y \leq 50 \text{ at\%}$
3. Component according to claim 1, characterized in that  $20 \text{ at\%} \leq y \leq 40 \text{ at\%}$
4. Component according to any of the previous claims 1 to 3 characterized in that the coating comprises a CrN layer deposited between the surface of the component and the MoxCryN layer.
5. Component according to any of the previous claims 1 to 4 characterized in that the component is an automotive component or a precision component.
6. Component according to any of the previous claims 1 to 5 characterized in that the surface of the component which is coated has a hardness equal or lower than 65 HRC.
7. Method for producing a component according to any of the previous claims, wherein the MoxCryN layer is deposited by means of a reactive PVD process
8. Method according to claim 6 characterized in that the reactive PVD process is a reactive Arc PVD process, wherein during deposition of the MoxCryN at least one target comprising Mo and Cr or at least one target comprising Mo and at least one target comprising Mo are evaporated by using Arc PVD techniques in an atmosphere comprising nitrogen as reactive gas.

Figures

Figure 1

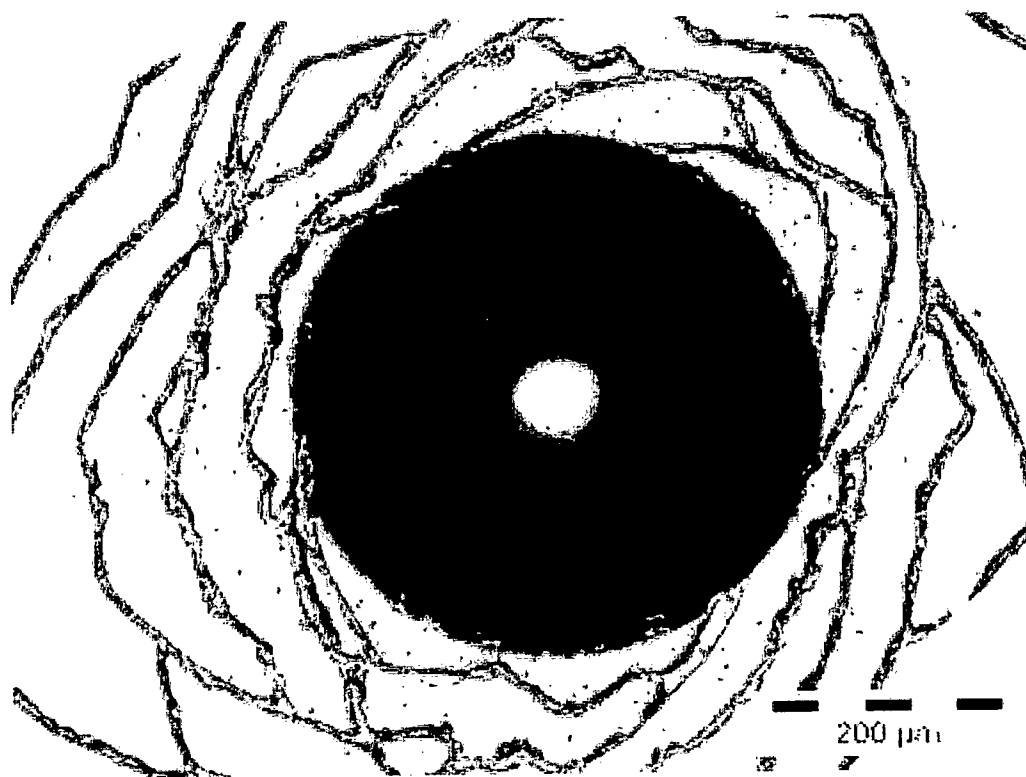


Figure 2

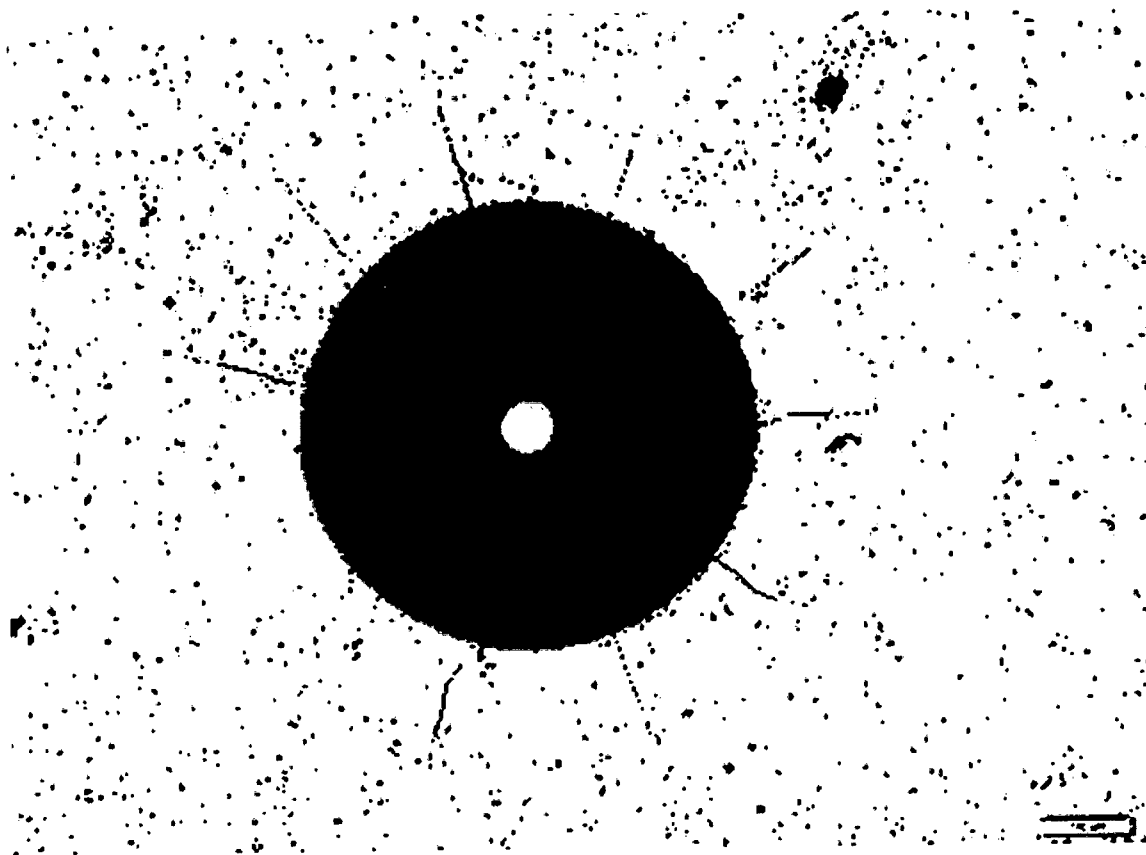
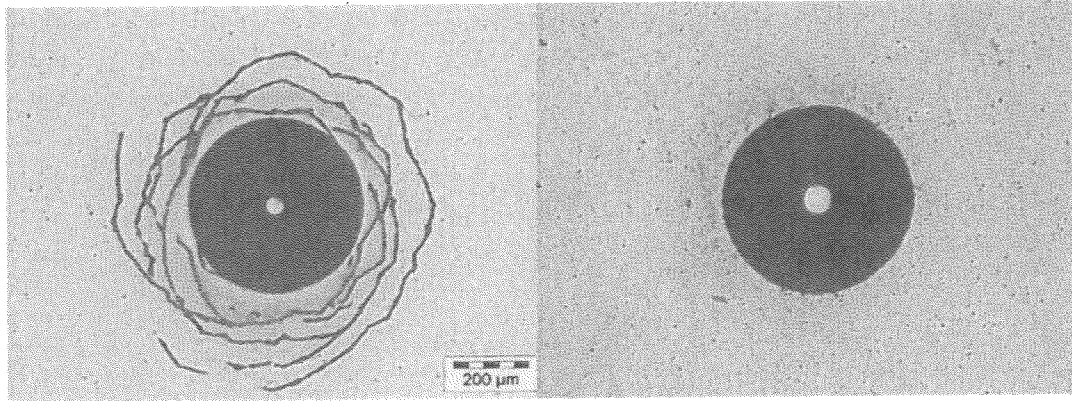
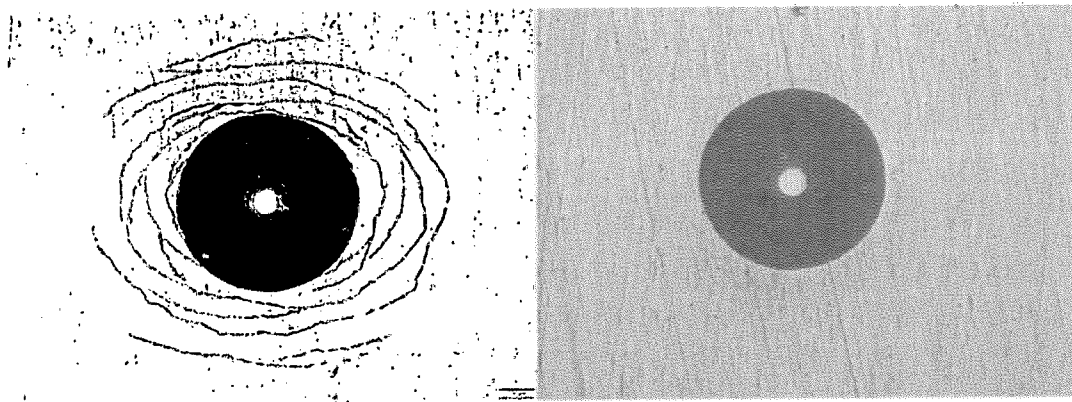


Figure 3



3a

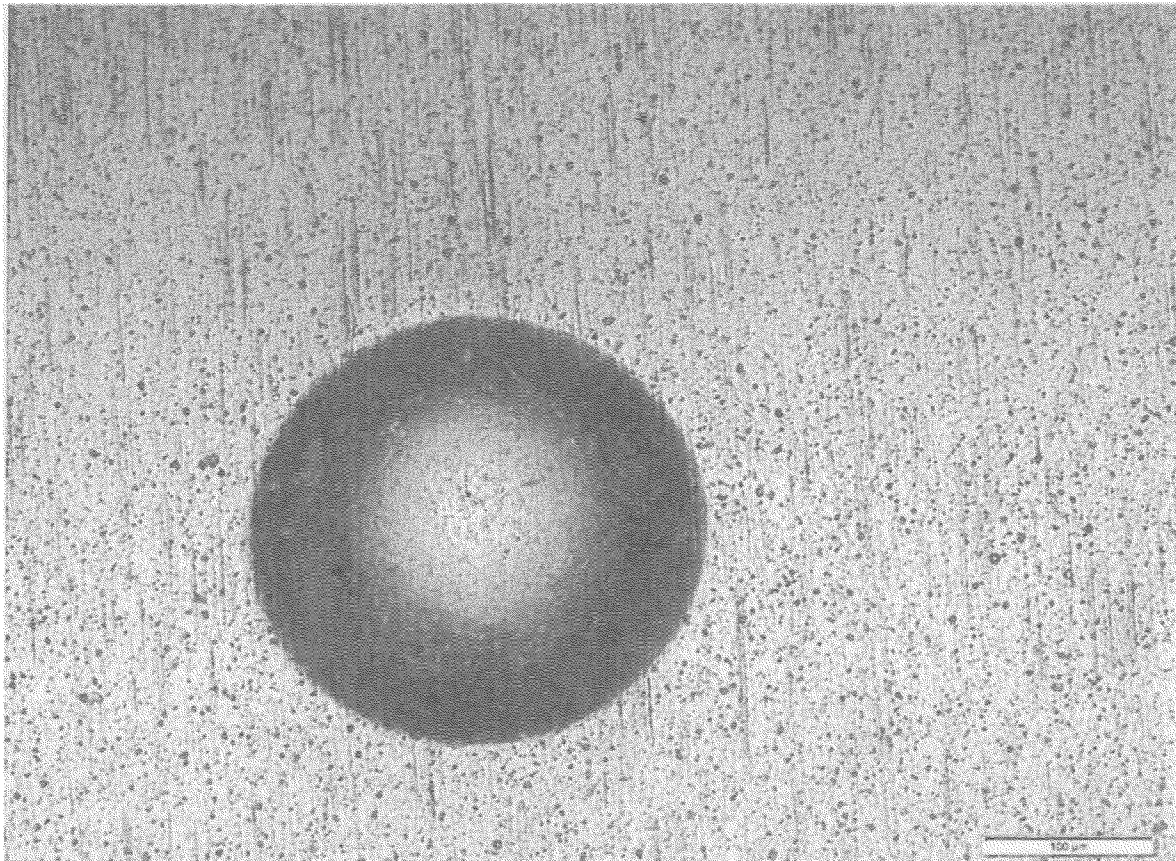
3c



3b

3d

Figure 4



INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2017/000437

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. C23C14/00 C23C14/06 C23C28/04 C23C30/00  
 ADD.  
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED  
 Minimum documentation searched (classification system followed by classification symbols)  
 C23C  
 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 601 293 A (FUKUTOME HIROTO [JP] ET AL) 11 February 1997 (1997-02-11)	1-3,5-8
Y	column 1, lines 45-55 - column 2, lines 48-54,65-67 column 3, lines 12-15,34 - column 9, lines 42-45	4
X	----- US 2013/134033 A1 (LYO IN WOONG [KR] ET AL) 30 May 2013 (2013-05-30) page 1, paragraph 12 - page 2, paragraphs 19,28,29 ----- -/--	1,5,7,8

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  15 June 2017	Date of mailing of the international search report  23/06/2017
---	--

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Boussard, Nadège
--	--

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2017/000437

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>YUJIAO ZOU ET AL: "Thermal stability and mechanical properties of sputtered Chromium-Molybdenum-Nitride (CrMoN) coatings", JOURNAL OF ACHIEVEMENTS IN MATERIALS AND MANUFACTURING ENGINEERING, vol. 37, no. 2, 1 December 2009 (2009-12-01), pages 369-374, XP055381134, page 370, paragraph 2.1 -----</p>	1,2
Y	<p>DE 10 2012 207814 A1 (MAHLE INT GMBH [DE]) 14 November 2013 (2013-11-14) page 2, paragraph 8 - page 3, paragraph 15 -----</p>	4

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/000437

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US 5601293	A	11-02-1997	GB 2296257 A	26-06-1996
			US 5601293 A	11-02-1997
-----				
US 2013134033	A1	30-05-2013	DE 102012211465 A1	06-06-2013
			KR 20130060544 A	10-06-2013
			US 2013134033 A1	30-05-2013
			US 2017009331 A1	12-01-2017
-----				
DE 102012207814	A1	14-11-2013	NONE	
-----				