

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

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 November 2002 (07.11.2002)

PCT

(10) International Publication Number
WO 02/088407 A1

- (51) International Patent Classification⁷: C22C 1/10, C23C 30/00, F16J 9/26
- (21) International Application Number: PCT/SE02/00503
- (22) International Filing Date: 18 March 2002 (18.03.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
0101089-1 27 March 2001 (27.03.2001) SE
- (71) Applicant (for all designated States except US): **KONCENTRA VERKSTADS AB** [SE/SE]; Linnégatan 5, S-413 04 Göteborg (SE).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): **ARAM, Mehdi** [SE/SE]; Krongdammsvägen 71, S-433 44 Partille (SE).
- (74) Agent: **AWAPATENT AB**; Box 11394, S-404 28 Göteborg (SE).
- (81) Designated States (national): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 02/088407 A1

(54) Title: NICKEL-ALUMINIDE BASED WEAR RESISTANT MATERIAL FOR PISTON RINGS

(57) Abstract: A piston ring comprises a coating of a wear-resistant composite composition, particularly intended for high temperature applications. The wear-resistant composite composition comprises a ceramic compound and at least 50 volume %, based on the total volume of the wear-resistant composition, of an intermetallic nickel-aluminide chosen from the group consisting of NiAl and Ni₃Al. A piston ring comprises a wear-resistant composite composition, particularly intended for high temperature applications. The wear-resistant composite composition comprises a ceramic compound and at least an intermetallic nickel-aluminide chosen from the group consisting of NiAl and Ni₃Al.

NICKEL-ALUMINIDE BASED WEAR RESISTANT MATERIAL FOR PISTON RINGS

WEAR-RESISTANT COMPOSITIONField of the Invention

The invention relates to a piston ring comprising a coating of a wear-resistant composite composition, particularly intended for high temperature applications, 5 the wear-resistant composite composition comprising a ceramic compound.

The invention further relates to a piston ring comprising a wear-resistant composite composition, particularly intended for high temperature applications, 10 the wear-resistant composite composition comprising a ceramic compound.

Technical Background

Very specific demands have to be met by high 15 temperature applications e.g. piston rings that are intended for use in for instance marine diesel engines, particularly as concerns strength, anti-corrosive properties, wear resistant, and material resilience. When used in a diesel engine the piston ring is arranged to 20 abut on the one hand against an associated piston groove, on the other against an engine cylinder-bore.

Consequently, the ring should be wear-resistant, particularly at the interface towards the cylinder bore, where high friction is generated when the engine is in 25 operation. The piston ring should therefore also possess an inherent tension or resilience whereby the piston ring will constantly be forced outwards, into abutment against the cylinder bore. In addition, upon each explosive stroke of the engine, the piston ring is urged with 30 considerable force radially outwards, into abutment against the cylinder bore, with consequential increase of stress. Due to a high working temperature in engines and especially due to the impact of produced heat, from contact between piston rings and cylinder liner during

the process, many materials loose some of their yield strength and show softening.

In operation, especially some contact areas between the piston ring and cylinder liner material are exposed
5 to high temperatures, to considerable temperature differences, and to the effects of a highly corrosive environment.

In order to withstand the effects of these stress-inducing causes, the piston ring therefore also must
10 exhibit considerable wear resistant, ductility, and thermal stability. By ductility is to be understood herein the maximum possible deformation of the material before cracking begin.

Today, piston rings are generally manufactured from
15 a cast-iron blank, which meets the requirements imposed on the material as regards strength and resilience but not on wear resistance on the surface thereof that faces the cylinder bore. Cast iron does not possess the required thermal stability at high temperature. A cast-
20 iron piston ring blank therefore usually is provided with a wear-resistant wear layer on the surfaces most exposed to wear.

The wear layer, which usually is formed by a chromium-compound material, is generally applied to the
25 piston ring blank in an electrolysis process as described e.g. in EP 0 668 375. In accordance with the teachings of this specification the piston ring blank is given a hard chromium layer in an electrolysis process. However, difficulties do arise in achieving a sufficiently strong
30 bond between the material of the blank and the material of the wear layer, which causes problems, because of the risk that the material of the wear layer be torn away from the material of the blank. When this happens, the comparatively soft material of the blank-material surface
35 is exposed to wear in the area of contact against the cylinder bore, with resulting considerable shortening of the life of the piston ring.

Another problem is that the coating gradually wears away, even if the bond between the surfaces is comparatively strong. The wear on the piston ring progresses slowly as long as the wear layer is intact but very rapidly, once that layer has disappeared. As a result, it may be difficult to determine in time when a piston ring change should be made.

Another issue is to increase the oxidation resistance of the piston ring at high temperatures. In WO9532314 there is provided a nickel-aluminium intermetallic basis alloy considered suitable for pieces, such as gas turbine blades, exposed to a high and continuous thermal stress. This alloy is claimed to improve thermal, oxidation and thermo-chock resistance. However, the hardness properties and wear-resistance of this compound are considered insufficient for use by other pieces and elements exposed to wear and thermal stress.

Summary of the Invention

The object of the present invention is to provide a material, particularly intended for medium to high temperature applications such as piston rings, that meets the requirements necessary as regards wear resistance, resilience, anti-corrosiveness, hardness, thermal stability and ductility.

Another object is to provide a piston ring, which does not suffer from the above drawbacks found in the prior art. Other features and advantages of the present invention will become apparent from the following description of the invention.

The present invention provides a wear-resistant composition, intended for medium to high temperature applications, particularly for piston rings, wherein the material comprises a composite ceramic compound (hard phase). Said composite composition also comprises at

least an intermetallic nickel-aluminide chosen from the group consisting of NiAl and Ni₃Al or a mixture thereof.

One of the advantages of the inventive wear-resistant composition is the ability to withstand yield strength softening up to a temperature of around 600 °C. It is not unusual that a piston ring locally has to withstand temperatures in the range of 400 to 500 °C or more in working conditions. If the metallic material (the matrix) in such a composite for some reason, e.g. softening caused by high temperature, can not withstand movement of the hard phase in the composite, the hard phase is not likely to stay in place. The hard phase will leave their place and then work like a polishing agent and cause higher wear (three body wearing).

It is thus beneficial to use an intermetallic nickel-aluminide for providing support to the ceramic compound in the composite material. An important object for the intermetallic nickel-aluminide is to keep the hard phase in place during contact with liner material in order to avoid the earlier described polishing effect even in the above-mentioned temperature range.

In a preferred embodiment of the present invention said composite composition comprises a matrix formed by the intermetallic nickel-aluminides from said group.

It is thus advantageous to use an intermetallic nickel-aluminide matrix for providing support to the ceramic compound in the composite material. An important object for the intermetallic nickel-aluminide matrix is to keep the hard phase in place.

The wear-resistant composition according to the invention also comprises a hard phase consisting preferably of at least a ceramic compound chosen from a group consisting of aluminium oxide, chromium carbide, chromium oxide and silicon carbide e.g. Al₂O₃, Cr₃C₂, Cr₂O₃, and SiC.

The hard phase improves the wear resistance and the ability to resist thermal fatigue deformation of the

composite. At the same time the coefficient of thermal expansion of the inventive composition is reduced. The compatibility of hard phase and matrix is an important factor in this case. Al_2O_3 is preferred due to higher interface bonding with the matrix material but the other hard phases are also working well in this respect.

It is also an object of the present invention to provide a piston ring, particularly intended for diesel engines, consisting of the inventive wear-resistant composition.

It is also provided in accordance with the present invention a piston ring, particularly intended for diesel engines, wherein said piston ring comprises a coating of the inventive wear resistant composition. By using the wear-resistant composition especially as coating on a substrate a more cost efficient product is obtained.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent for one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof. Thus it is understood that various methods such as plasma-, HVOF spraying or other related prior art methods can be used to apply the inventive composition to a substrate such as e.g. a piston, a piston ring and a cylinder liner or at least parts of them.

Brief Description of the Drawing

Currently preferred embodiments of the present invention will now be described in more detail, with reference to the accompanying drawing.

Fig. 1 is a schematic representation of superlattice dislocations in a two-dimensional simple cubic lattice.

Fig. 2 is a table showing the rate of wear relative to pressure-exposure in tests of a composition in accordance with one embodiment of the invention vis-à-vis a well-known cast iron for piston rings named Darcast.

Fig. 3 is a SEM-picture of a composition in accordance with the invention.

Fig. 4 is one embodiment of a piston ring in accordance with the present invention.

5

Detailed Description of Preferred Embodiments

In accordance with a preferred embodiment of the invention it is provided a wear-resistant composite composition, intended for medium to high temperature applications and particularly for piston rings, wherein the wear-resistant composite composition comprises a ceramic mixture of intermetallic composition and a ceramic compound. The wear-resistant composite composition specifically comprises at least one intermetallic nickel-aluminide chosen from the group consisting of NiAl and Ni₃Al. The intermetallic nickel-aluminide or nickel-aluminides forms a matrix to which a hard phase is added.

As used herein the term intermetallic compounds are a class of materials, which can be viewed as occupying an intermediate position regarding the properties of the material between metallic alloys and ceramics. They are also considered as a unique class of metallic materials that form long-range ordered crystal structures below a critical temperature, generally referred to as the critical ordering temperature (T_c).

The essential condition for a substitutional solid solution of a suitable composition to become ordered is that unlike atoms i.e. different elements must attract each other more than like atoms in order to lower the free energy upon ordering. In other words, the degree of order of intermetallic compounds is closely related to the nature of the bonding. These ordered intermetallics usually exist in relatively narrow compositional ranges around simple stoichiometric ratio.

The ordered crystal structure of nickel aluminides makes it feasible to achieve high tensile ductility. The

ductility of polycrystalline Ni₃Al is further increased by micro alloying with boron addition that segregates the grain boundaries and suppresses brittle intergranular fraction.

5 An above-mentioned effect depending on the crystal structure is represented schematically in Fig. 1 by a super lattice dislocation in a two-dimensional simple cubic lattice. Intermetallic compounds exhibit a very high yield stress that is often maintained to elevated
10 temperatures. Deformation in ordered alloys is controlled by the glide of super lattice or paired dislocations, as super dislocations, further illustrated in Fig. 1 for a two-dimensional ordered lattice having an AB composition. The first, or leading, dislocation creates a layer of
15 anti-phase domain, which can be thought of simply as a layer of wrong bonding, and the second, or following, dislocation restores the order. The relatively low mobility of super dislocations gives higher yield strength; that is, yield strength increases rather than
20 decreases with increasing temperature.

The wear-resistant composition comprises a matrix formed by an intermetallic nickel-aluminide chosen from a group consisting of NiAl and Ni₃Al. The composition also comprises a ceramic compound chosen from a group
25 consisting of chromium carbide, chromium oxide and aluminium oxide e.g. Cr₂O₃, Cr₃C₂, SiC and Al₂O₃.

Examples of embodiments of the present invention are given below.

30 Example 1

A composition was prepared by forming a mixture of the following ingredients in the parts by weight quoted in Table 1:

Table 1

35

No.	Name	Element	Ni	Al	Cr	Zr	Nb
1	NiAl-Nb	wt%	65-66	27-28	2-3	0,5-1	4-4,5

A powder was prepared by forming the mixture of components as set out in table 1 of example 1. Furthermore, 5-10% by volume of the initial mixture was replaced by 5-10% by volume of Al₂O₃. The resulting composition was heated and applied to a substrate in accordance with prior art techniques to form a wear-resistant composition on the substrate. The resulting composite had good wear resistance, ductility, and thermal stability properties.

Fig. 2 is a figure showing the rate of wear relative to pressure-exposure in tests of a composition in accordance with one embodiment of the invention vis-à-vis a well-known cast iron for piston rings known as Darcast.

In order to further illustrate the properties of the invention, reference is made to Fig. 3, which is an SEM-picture of a preferred embodiment of a wear-resistant composition in accordance with the invention. The picture discloses a matrix comprising darker "islands" of a hardphase. In this case the hardphase is a chromium carbide. By means of diffusion between matrix and hardphase a mixed zone, which is also clearly visible on the picture, is formed. The mixed zone provides for that a hard bonding is formed between hardphase and matrix and preferably the mixed zone is formed symmetrically around the hardphase.

A further embodiment of the wear-resistant composition according to the invention is outlined in the following example 2.

30 Example 2

Table 2

No.	Name	Element	Ni	Al	Fe	Mn	Ti	Zr	B
2	Ni3Al-Fe	wt%	77-78	9-10	11-12	0,5	0,5	0,01	0,1

35 A powder was prepared by forming an initial mixture of components as set out in table 2 of example 2.

Furthermore, 5-10% by volume of the initial mixture was replaced by 5-10% by volume of Al₂O₃. The resulting composition was exposed to heat treatment and applied to a substrate in accordance with e.g. prior art techniques to form a wear-resistant composition on a substrate. The resulting composite had good wear resistance, ductility, and thermal stability.

Example 3

A third example of a wear-resistant composition according to the invention is given in the below table.

Table 3

No.	Name	Element	Ni	Al	Cr	C	Mn	Ti	Zr	B
3	Ni3Al-Cr	wt%	81-83	8-9	7-8	0,1	0,4-0,5	1	0,6	0,1

15

A wear resistant composition was prepared by forming the mixture of components as set out in Table 3 of example 3. In this example chromium carbide is used as hard phase compared to the previous given examples. By, in accordance with the previous examples adding the hard phase Al₂O₃ to the mixture in table 3 instead, an increased thermal stability is obtained compared to the mixture according to table 3. Though Al₂O₃ is given as the preferred alternative for a hard phase compound in the above stated examples, excellent results were achieved with other hard phase compounds as well.

It is of course possible to use any hard phase from the group consisting of chromium carbide, chromium oxide, silicon carbide and aluminium oxide e.g. Cr₂O₃, Cr₃C₂, SiC and Al₂O₃ in combination with any composition given in the tables 1-3.

Fig. 4 is one embodiment of a piston ring in accordance with the invention. The piston ring preferably comprises a coating of said wear-resistant composition. In a second preferred embodiment of the invention the

35

piston ring consists of the inventive wear resistant composition.

As will be appreciated, the present invention is not limited to the embodiments and examples described herein. For example, further substances may be added to the wear-resistant composition in order to modify its properties in some respect. Also other mixtures and combinations than those listed in the tables 1-3 are possible within the scope of the invention. For special conditions up to 50 %, preferably between 1-30 %, and most preferably between 5-10 % by volume of the total composition can be hard phase such as, chromium oxide, silicon carbide, Cr_3C_2 and Al_2O_3 .

CLAIMS

1. A piston ring comprising a coating of a wear-resistant composite composition, particularly intended for high
5 temperature applications, the wear-resistant composite composition comprising a ceramic compound, c h a r a c -
t e r i z e d in that said wear-resistant composition also comprises at least 50 volume%, based on the total
volume of the wear-resistant composition, of an
10 intermetallic nickel-aluminide chosen from the group consisting of NiAl and Ni₃Al.
2. A piston ring according to claim 1, wherein said composition comprises a matrix formed by an intermetallic
15 nickel-aluminide chosen from said group consisting of NiAl and Ni₃Al.
3. A piston ring according to claim 1 or 2, wherein the intermetallic nickel-aluminide is a mixture of NiAl and
20 Ni₃Al.
4. A piston ring according any one of claims 1-3, wherein the ceramic compound is Cr₃C₂.
- 25 5. A piston ring according to any one of claims 1-3, wherein the ceramic compound is a chromium oxide, such as Cr₂O₃.
6. A piston ring according to any one of claims 1-3,
30 wherein the ceramic compound is SiC.
7. A piston ring according to any one of claims 1-3, wherein the ceramic compound is aluminium oxide, such as
Al₂O₃.
35
8. A piston ring according to any one of claims 1-7, wherein the composition preferably comprises between 70-

99 volume% intermetallic nickel-aluminide based on the total volume of the wear-resistant composition.

9. A piston ring according to any one of claims 1-7,
5 wherein the composition preferably comprises between 90-95 volume% intermetallic nickel-aluminide based on the total volume of the wear-resistant composition.

10. A piston ring comprising a wear-resistant composite
10 composition, particularly intended for high temperature applications, the wear-resistant composite composition comprising a ceramic compound, c h a r a c
t e r i z e d in that said wear-resistant composition also comprises at least an intermetallic nickel-aluminide
15 chosen from the group consisting of NiAl and Ni₃Al.

11. A piston ring according to claim 10, wherein said
composition comprises a matrix formed by an intermetallic
nickel-aluminide chosen from said group consisting of
20 NiAl and Ni₃Al.

12. A piston ring according to any one of claims 10-11,
wherein the intermetallic nickel-aluminide is a mixture
of NiAl and Ni₃Al.

25

13. A piston ring according any one of claims 10-12,
wherein the ceramic compound is Cr₃C₂.

14. A piston ring according to any one of claims 10-12,
30 wherein the ceramic compound is a chromium oxide, such as Cr₂O₃.

15. A piston ring according to any one of claims 10-12,
wherein the ceramic compound is SiC.

35

16. A piston ring according to any one of claims 10-12, wherein the ceramic compound is aluminium oxide, such as Al_2O_3 .
- 5 17. A piston ring according to any one of claims 10-16, wherein the composition comprises at least 50 volume% intermetallic nickel-aluminide based on the total volume of the wear-resistant composition.
- 10 18. A piston ring according to any one of claims 10-17, wherein the composition preferably comprises between 70-99 volume% intermetallic nickel-aluminide based on the total volume of the wear-resistant composition.
- 15 19. A piston ring according to any one of claims 10-17, wherein the composition preferably comprises between 90-95 volume% intermetallic nickel-aluminide based on the total volume of the wear-resistant composition.

1/4

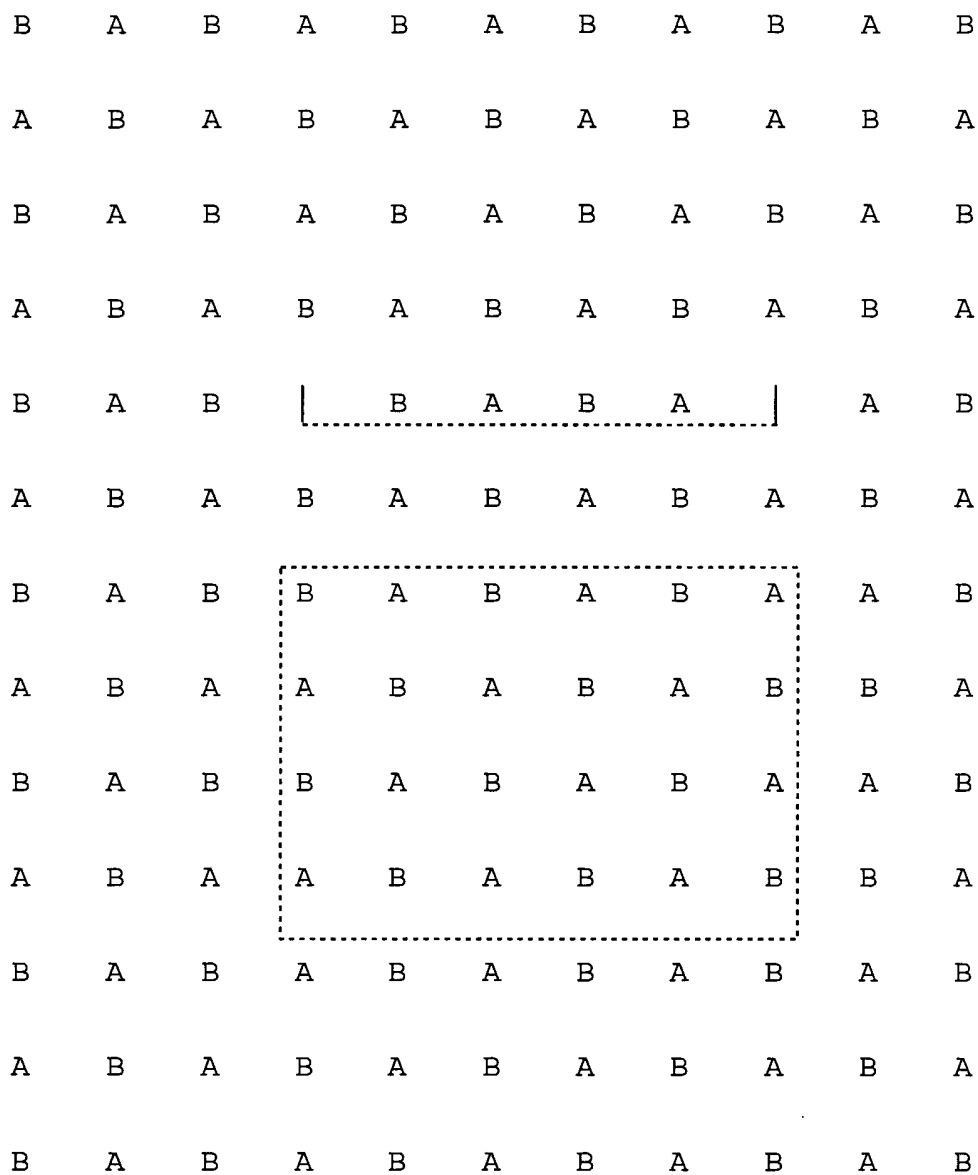


Fig. 1

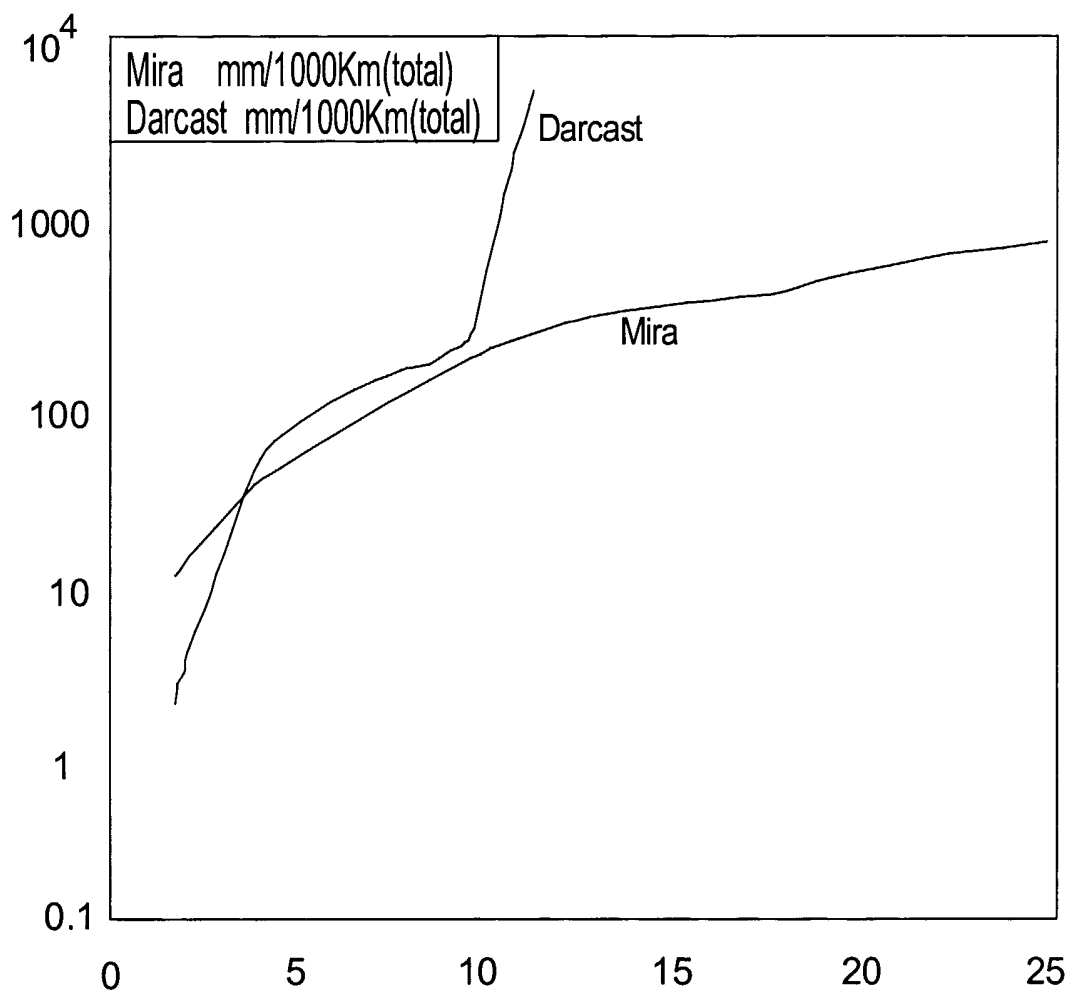


Fig. 2

3/4

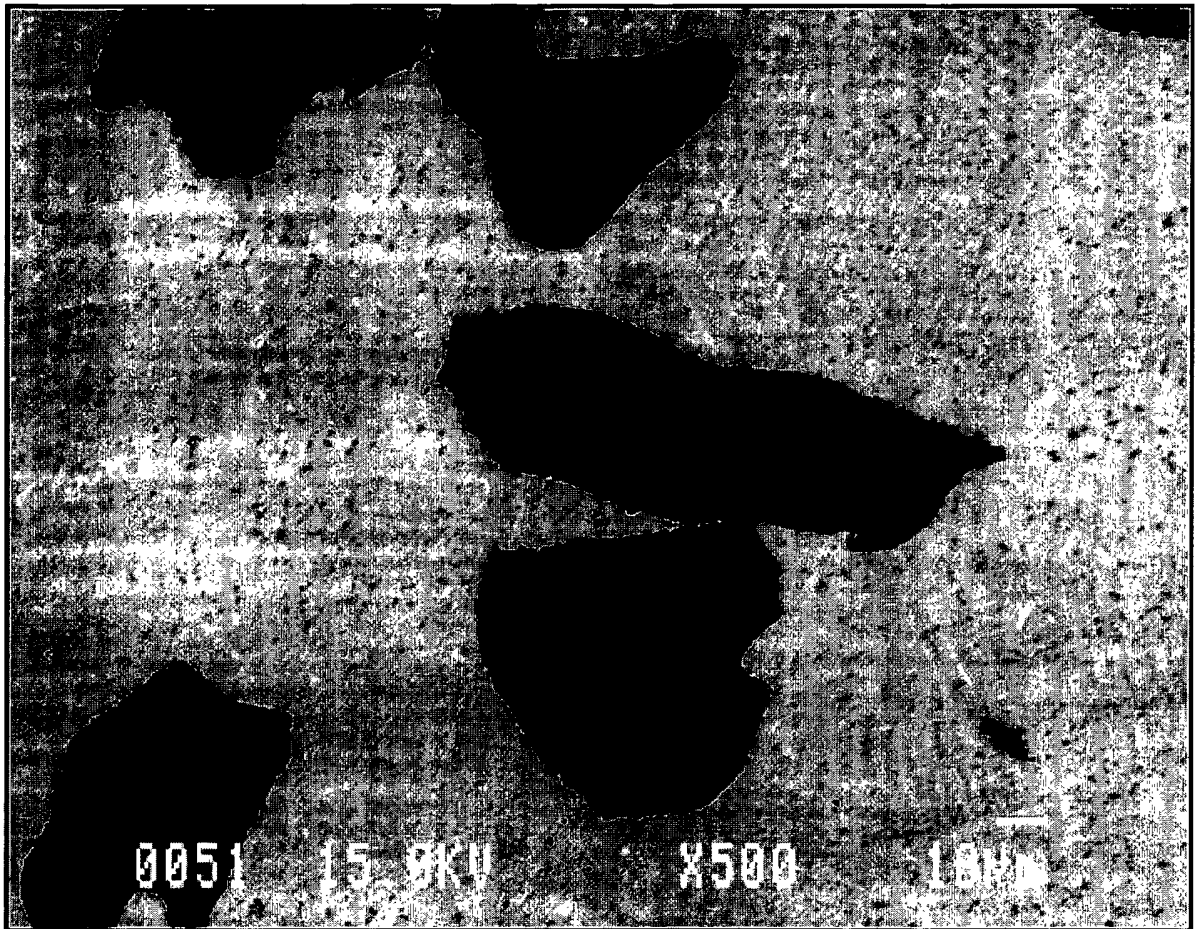


Fig. 3

4/4

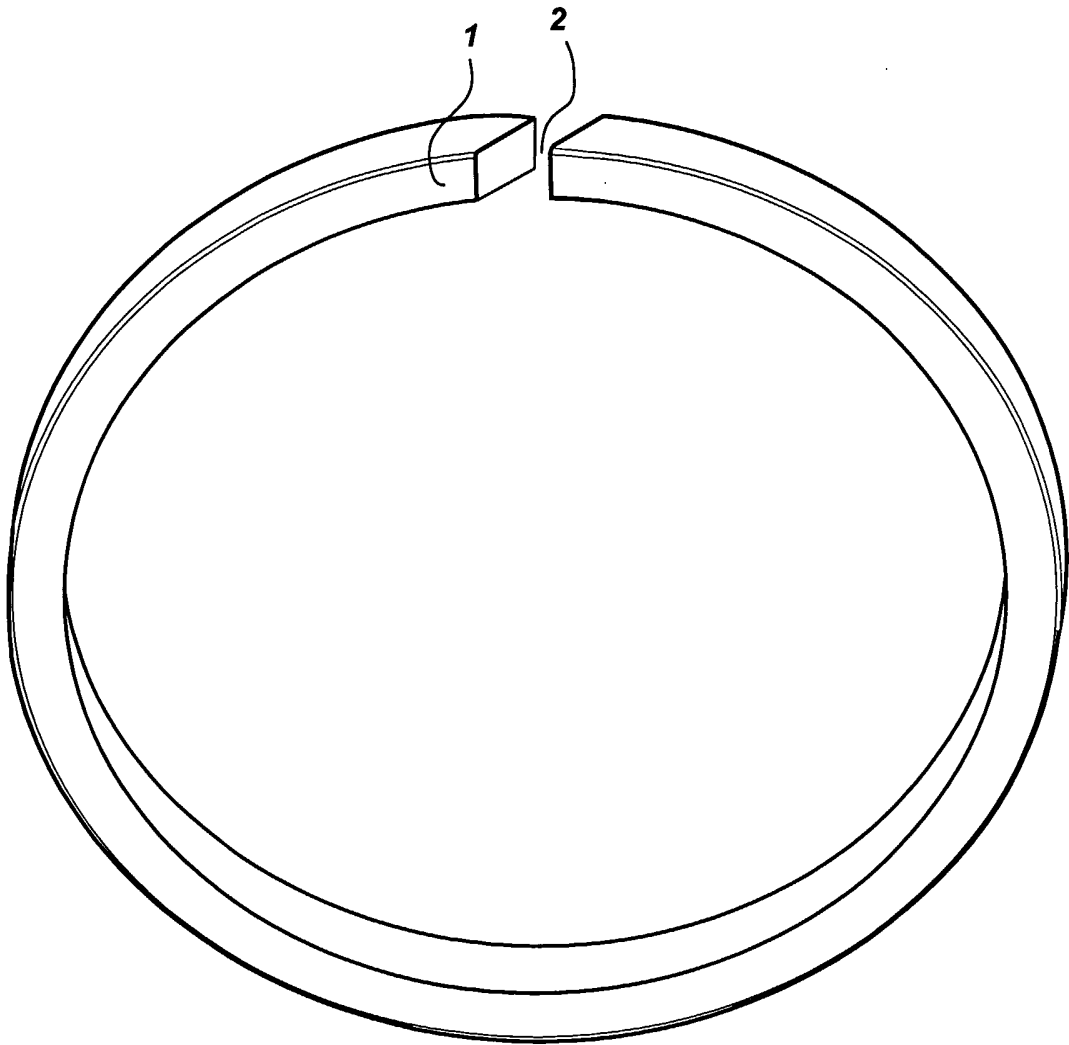


Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 02/00503

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C22C 1/10, C23C 30/00, F16J 9/26
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)

IPC7: C22C, F16J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0645463 A2 (HONDA GIKEN KOGYO KABUSHIKI KAISHA), 29 March 1995 (29.03.95), page 2, line 54 - page 3, line 36; page 6, line 49 - page 7, line 15 --	1-9,10-19
Y	US 5743012 A (ADAMS ET AL), 28 April 1998 (28.04.98) --	1-9,10-19
Y	US 5281484 A (TANK ET AL), 25 January 1994 (25.01.94) --	1-9,10-19
A	WO 9532314 A1 (SIEMENS AKTIENGESELLSCHAFT), 30 November 1995 (30.11.95) --	1-9,10-19

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"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	Date of mailing of the international search report
25 June 2002	04-07-2002

Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Nils Engnell/SN Telephone No. +46 8 782 25 00
--	---

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 02/00503

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6025065 A (CLAUSSEN ET AL), 15 February 2000 (15.02.00) -- -----	1-9,10-19

INTERNATIONAL SEARCH REPORT
Information on patent family members

01/05/02

International application No.

PCT/SE 02/00503

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0645463 A2	29/03/95	DE 69407525 D,T JP 7243020 A JP 7083330 A	16/04/98 19/09/95 28/03/95
US 5743012 A	28/04/98	DE 3861882 D EP 0284118 A,B GB 2201484 A,B GB 8704325 D GB 8803899 D	00/00/00 28/09/88 01/09/88 00/00/00 00/00/00
US 5281484 A	25/01/94	DE 4203869 A,C GB 2264079 A,B GB 9302473 D JP 2037164 C JP 6212455 A JP 7056077 B	12/08/93 18/08/93 00/00/00 28/03/96 02/08/94 14/06/95
WO 9532314 A1	30/11/95	CN 1044493 B CN 1150826 A CZ 9603426 A DE 4417936 C DE 59509221 D EP 0760869 A,B SE 0760869 T3 JP 10500453 T RU 2148671 C US 5935349 A	04/08/99 28/05/97 13/08/97 07/12/95 00/00/00 12/03/97 13/01/98 10/05/00 10/08/99
US 6025065 A	15/02/00	DE 4447130 A DE 59504520 D EP 0800495 A,B JP 10511071 T WO 9620902 A	04/07/96 00/00/00 15/10/97 27/10/98 11/07/96