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(54) Title: ARTICLE WITH WEAR- RESISTANT COATING AND METHOD OF FORMING SAME

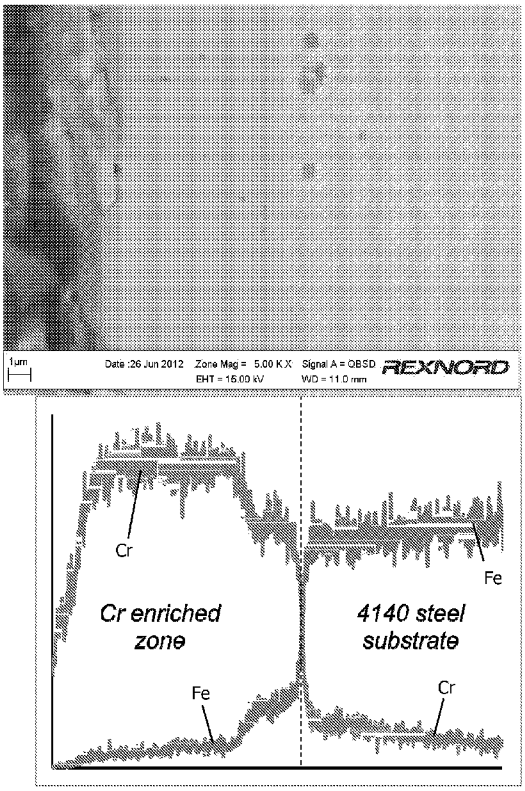

FIG. 1

(57) Abstract: An article with a wear-resistant coating and a method for forming this wear-resistant coating using pack cementation are disclosed. According to one form, a chromium diffusion layer is formed on a ferrous substrate material to improve hardness and improve the wear resistance of a sliding contact surface.

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ARTICLE WITH WEAR-RESISTANT COATING AND METHOD OF FORMING SAME

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. provisional patent application no. 61/533,948 entitled "Article with Wear-Resistant Coating and Method of Forming Same" filed on September 13, 2011. The content of that application is hereby incorporated by reference as if set forth in its entirety herein.

BACKGROUND

[0002] This disclosure relates to wear-resistant coatings and methods of forming such coatings for bearing applications.

[0003] When two surfaces bear on one another, the interaction between the surfaces can result in displacement of the material of the surfaces caused by abrasion, adhesion, or erosion. When such interaction occurs for a sufficiently long period of time and/or under a sufficiently high load, wear of the surfaces may occur. This wear can plastically deform the surfaces and cause, among other things, dimensional inaccuracy of the component(s), an increased susceptibility to corrosion, and an increased likelihood of the formation of debris or micro-cracking that can instigate failure of the underlying component(s).

[0004] For some applications, coatings have been applied to the bearing surfaces to improve their resistance to wear and to improve their frictional properties. However, these coatings may chip or mechanically delaminate from the underlying substrate. Once the coating is damaged, the effectiveness of the coatings is reduced and the integrity of the component(s) is potentially compromised.

[0005] Hence, there remains a need for improved coatings and for ways to reduce the wear of bearing surfaces.

SUMMARY

[0006] Disclosed herein are an article with a wear-resistant chromium diffusion coating and a method for forming this wear-resistant chromium diffusion coating using pack cementation. This coating process might be used to improve wear resistance during service of bushings, bearings, the teeth of gears, pins on chain links for conveying surfaces, and so forth.

[0007] Previously, pack cementation has been used in the preparation of aerospace components as a thermal barrier coating and was performed at greater temperatures than are described in this application. In such situations, the treatment was used to create an oxidation resistant layer that would protect the underlying metallic alloy under extreme temperature conditions.

[0008] According to one method of making the wear-resistant coating for a bearing application, a ferrous substrate material is packed into a powder that includes chromium to be transferred to the ferrous substrate material. The chromium to be transferred to the ferrous substrate is reacted with a halide salt, such as NaF or NH_4Cl, to form a metal-halide vapor species. This metal-halide vapor species contacts the ferrous substrate material and the chromium is transferred to the ferrous substrate material. The chromium diffuses into the surface of the ferrous substrate material, thereby forming the wear-resistant coating on the ferrous substrate material.

[0009] As formation of the chromium diffusion layer using pack cementation relies on the diffusion of the chromium into the ferrous substrate material, the formed diffusion layer is less susceptible to failure modes such as, for example, delamination and chipping, that are common to mechanically-applied coatings.

[0010] Moreover, unlike some other chemical deposition processes, such as chromium electroplating which can present health and environmental risks if not properly contained, pack cementation is a comparably clean process.

[0011] In some forms, this method may be used to enrich a bearing surface of, for example, a ferrous alloy.

[0012] In some forms, the chromium diffusion layer may contain intermetallic phases which further enhance the material properties of the wear-resistant coating, thereby improving its in-service performance. Due to their increased coherence with the substrate material, such intermetallic phases may further inhibit the movement of material from the coated component when the article is subjected to sliding friction and thereby reduces wear.

[0013] Additionally, an article comprising a wear-resistant coating may be made according to the methods described herein.

[0014] These and still other advantages of the invention will be apparent from the detailed description. What follows is merely a description of some preferred embodiments of the present invention. To assess the full scope of the invention the claims should be looked to as the preferred embodiments are not intended to be the only embodiments within the scope of the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIG. 1 is an SEM image of a chromium diffusion coating on a 4140 steel substrate prepared using 55 wt% chromium and 2.5wt% NH_4Cl as the halide salt activator in the pack powder at 1000°C processing conditions as described in the example below. The SEM image was taken in backscattered imaging mode to evaluate the coating thickness and homogeneity along with an associated EDS line scan that illustrates the compositional gradient of chromium and iron.

[0016] FIG. 2 is a bulk outer surface scan of the coating on a 4140 steel substrate prepared using 55 wt% chromium and

2.5 wt% NH_4Cl as the halide salt activator in the powder at 1000°C processing conditions as described in the example below.

[0017] FIG. 3 is an SEM image of a chromium diffusion coating on a 4140 steel substrate that was prepared using 55 wt% chromium and 2.5 wt% NH_4Cl as the halide salt activator in the powder at 850°C processing conditions as described in the example below.; and

[0018] FIG. 4 is an SEM image of a chromium diffusion coating on a 52100 steel substrate that was prepared using 39 wt% chromium and 2.5wt% NaF as the halide salt activator in the pack powder at 800°C processing conditions as described in the example below.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019] Pack cementation is an *in situ* batch diffusion coating process whereby the article to be coated is initially buried in a refractory container that is filled with a thoroughly mixed powder pack. The powder pack contains a powder of the chosen diffusion element or a master alloy composition, an inert filler powder (e.g., Al_2O_3, SiO_2, or SiC), and a halide salt activator. The refractory container holds the article comprising the substrate material buried in the powder pack mixture and is covered with a refractory lid. This covered refractory container is placed in a furnace and heated to a temperature ranging from 600 to 1200°C.

[0020] To prevent the metal powder present in the pack from oxidizing during high temperature exposure, a continuous stream of an inert gas (e.g., Argon) is purged through the furnace chamber. When the powder pack is exposed to the elevated temperature, the diffusion element or the master alloy composition reacts with the halide salt to form a metal-halide vapor species. The metal-halide vapor species diffuses through the porous powder pack to the substrate material where the metal ion species is reduced to allow for its diffusion into the surface of the substrate material.

[0021] The halide-activated pack cementation process recited herein may be applied to enrich the surface of ferrous substrate materials that experience sliding wear during in-service application with a chromium diffusion coating. By diffusing the chromium into the ferrous substrate material, the final coated article realizes a reduction in sliding wear rate compared to a similar uncoated article.

[0022] Given that the wear-resistant coating is formed by a diffusive process, it should be appreciated that the properties of the coating (e.g., thickness, morphology, and so forth) may be modified by altering the various process parameters such as, for example, the temperature of the furnace, the thermal profile of the part over the duration of the process, the properties of the substrate material itself, and the rate of gaseous flow through the powder pack.

[0023] In some forms, the pack cementation method may produce a strong compositional enrichment at the substrate surface, leading to inward formation of an intermetallic phase from the original substrate surface.

[0024] It will be appreciated that this type of diffusion coating is predicated on the formation of a chemical diffusion zone to bond the compositionally graded chromium-enriched surface to the bulk ferrous substrate material. The chemical bond between the wear-resistant chromium coating and ferrous substrate material formed by diffusion is different from a mechanical bond that is typically present on a coating physically deposited onto a substrate. Indeed, the chemical gradient between the chromium-enriched diffusion coating and the bulk of the ferrous substrate material in the pack cementation process has increased coherency and is not susceptible to potential coating delamination caused by mechanical or thermal mismatch at a substantially more incoherent interface between a mechanically deposited coating and its corresponding substrate. Relative to the robust interfacial integrity between a pack cementation diffusion coating and the original substrate, the increased interfacial stress between a mechanically bonded coating and its respective substrate during a typical sliding wear operation could result in spalling or delamination of the coating and accelerated reduction in system performance.

[0025] In specific comparison to electrodeposition of chromium onto a metal substrate for improved tribological properties, a chromium or chromium alloy diffusion coating created by the halide-activated pack cementation method is uniform in thickness and free from microcracking that is inherent to the chromium electrodeposition process. By adjusting the process parameters of the pack cementation coating process, the ability to tailor the microstructure and composition of the diffusion coating to improve the wear behavior of the original substrate material is gained.

[0026] Halide activated pack cementation is an example of the process or method used to deposit a chromium layer onto steel samples for the purpose of establishing a sliding contact surface or bearing layer. The formation of a surface of this type may be particularly advantageous on, for example, a radially inward facing surface of a bushing or on a bearing surface of a race part for a bearing.

[0027] This example is offered for illustrative purposes only, and is not intended to limit the scope of the present invention in any way. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description and the following example and fall within the scope of the appended claims.

EXAMPLE

[0028] Pack cementation was performed under a variety of conditions on steel samples to create a chromium diffusion layer using a 2^3 factorial design of experiment. Samples were prepared and run at processing or deposition temperatures of either 800°C or 1000°C, using a halide salt activator of either NaF or NH_4Cl, and with either 39 or 50 weight percent chromium in the pack.

[0029] First, sample coupons (1 cm x 1 cm x 1 cm) were cut from bar stock of AISI 4140 steel and AISI 52100 steel. The surfaces of these samples were prepared using 600 grit SiC paper to remove extraneous oxide at surface of these samples and then subjected to ultrasonication in isopropyl alcohol.

[0030] The samples were prepared for pack cementation. An alumina crucible was obtained and filled with a mixed powder. In these trials, the pack powder consisted of either approximately 39 or 50 weight percent of chromium and approximately 3 weight percent of the halide salt activator (which was either NaF or NH_4Cl depending on the run) with the remainder of the powder being a reactively inert filler.

[0031] It should be noted that, while the weight percent chromium was varied, it did not serve as a limiting factor in the reaction. Accordingly, the test results below are primarily of interest for the effect of the halide salt activator type and temperature on the layer formed.

[0032] The prepared steel samples were buried in the powder within the alumina crucible, the crucible was covered, and filled crucible was placed within a furnace for processing. Initially, the filled crucible was placed in the furnace at 260°C and held at that temperature for 1 hour to bake off any residual moisture present in the pack powder. Argon is used as a purge gas to create inert atmosphere within the furnace. After the 1 hour bake, the temperature of the furnace was elevated to start the deposition process. Depending on the run, this temperature was either 800°C or 1000°C. Because of constraints on the furnace, some amount of ramping time was required in order to obtain this target processing temperature. Typically this ramp up time was approximately 40 minutes. The samples were then held at this temperature for 12 hours to allow for the chromium metal to react with the halide salt activator and form a metal enriched gaseous phase, which then diffused into the surface of the substrate to form a Cr diffusion layer on the surface of the substrate.

[0033] After 12 hours of time at the processing or deposition temperature, the furnace was turned off and the samples were allowed to cool for 4 hours, thus giving a total processing time of approximately 16 hours. Once the furnace was substantially cooled, the crucible was removed from the furnace, and the argon purge gas was turned off. The prepared samples were removed from the packed crucible and were cut and mounted for metallographic examination and nanoindentation measurements.

[0034] To evaluate coating thickness and homogeneity, a cross section of the samples was evaluated using a Zeiss EVO 50 SEM in backscattered electron imaging mode. In some instances, EDS line scans were taken through the diffusion zone thickness to assess compositional gradients using an iXRF energy dispersive x-ray spectroscopy system with silicon drift detector.

[0035] Referring to FIG. 1, it can be seen that a chromium diffusion layer approximately 10 μm thick has been formed on the AISI 4140 steel substrate prepared using 55 wt% chromium and 2.5 wt% NH_4Cl as the halide salt activator in the pack powder at 1000°C processing conditions. The left side of FIG. 1 is the coated surface of the part, such that moving rightward there is the chromium diffusion layer, followed by the underlying substrate material. Below the image, is an energy dispersive x-ray spectroscopy (EDS) line scan taken across the interface between the chromium enriched zone and the 4140 steel substrate. The chemical spectrum information clearly indicates that the chromium (Cr) content is higher relative to iron (Fe) in the chromium enriched zone. The growth of the chromium enriched zone is controlled by the diffusion rate of chromium into the 4140 steel alloy.

[0036] FIG. 2 provides a bulk outer surface scan of a chromium coating of a 4140 steel substrate prepared using 55 wt% chromium and 2.5 wt% NH_4Cl as the halide salt activator in the powder at 1000°C processing conditions. This scan indicates that the surface of the coating is 99% chromium and 1% iron and thereby establishes that the treated surface is primarily chromium.

[0037] FIG. 3 provides another SEM image of the AISI 4140 steel with chromium diffusion coating, albeit at a lower magnification. In this image, the upper half of the image is the mounting material and the bottom half the substrate material. Because this image is in cross-section, the coating therefore runs horizontally across the image. At this level of magnification, what is notable is that the chromium coating is very homogenous, free of cracks, and of even thickness across the surface of the steel substrate.

[0038] FIG. 4 shows an SEM image of the AISI 52100 steel substrate that was prepared using 39 wt% chromium and 2.5 wt% NaF as the halide salt activator in the pack powder at 800°C processing conditions. The AISI 52100 steel coupon was coated with the chromium diffusion layer. Again, the evenness of the thickness of the chromium enriched zone, which runs horizontally across the image, is to be noted.

[0039] The mechanical properties of the diffusion layer were assessed using nanoindentation. Nanoindentation was performed using continuous stiffness measurement (CSM) mode to assess hardness and modulus of the diffusion zone relative to the substrate. Three replicate measurements were taken per sample to increase statistical significance of results. These tests were run with on an Agilent Technologies G200 nanoindenter with high load and CSM capability.

[0040] Additionally, a linear reciprocating tribometer was used to assess whether there was a change in wear rate associated with varying the parameters used to form the chromium diffusion layer. Sliding wear measurements were obtained using a linear reciprocating pin-on-disk (POD) tribometer to assess the friction coefficient and wear rate of coated samples relative to an uncoated baseline sample. The counterbody material was a 100Cr6 (AISI 52100) steel. The test machine was a CSM Instruments tool.

[0041] Table I below provides a comparison of the hardness and wear rates for the original (uncoated) substrates and for the chromium-coated samples.

TABLE I

Substrate material	**Hardness of Substrate [GPa]**	**Wear rate of substrate [$mm^3/N/m$]**	**Hardness of Coating [GPa]**	**Wear rate of Coating [$mm^3/N/m$]**
AISI 4140 steel	3.7 ± 0.9	4×10^{-4}	19.9 ± 1.3	2×10^{-5}
AISI 52100 steel	5.2 ± 0.3	6×10^{-4}	18.9 ± 0.8	2×10^{-5}

[0042] These results indicate that, prior to pack cementation, the AISI 52100 steel has a higher hardness and a higher wear rate than the AISI 4140 steel. However, the measured hardness of the chromium coatings on the two steel substrate types are virtually equal to one another and the wear rate of the chromium coating for the two steel substrate types are equal to one another.

[0043] Tables II and III below provide further indentation and wear rate data obtained for coated and uncoated AISI 4140 steel.

TABLE II

Indent location	**Avg Hardness [GPa]**	**Avg Modulus [GPa]**
Cr diffusion layer	19.9 ± 1.3	286.1 ± 11.2
4140 steel	3.7 ± 0.9	227.8 ± 9.5

[0044] Table II illustrates that the surface hardness is increased five-fold by application of a chromium diffusion layer. This represents a significant and appreciable improvement in hardness.

TABLE III

Material	**Wear rate of counterbody [$mm^3/N/m$]**	**Wear rate of material [$mm^3/N/m$]**
Cr diffusion layer	2×10^{-6}	2×10^{-5}
4140 steel	4×10^{-7}	4×10^{-4}

[0045] Table III indicates that the wear rate of the 4140 steel substrate against a 52100 steel counterbody is decreased by an order of magnitude with the application of a chromium diffusion coating to the substrate. Again, this is a significant and promising difference obtained by the application of the chromium coating.

[0046] Tables IV and V below provide further indentation and wear rate data obtained for coated and uncoated AISI 52100 steel.

TABLE IV

Indent location	**Avg Hardness [GPa]**	**Avg Modulus [GPa]**
Cr diffusion layer	18.9 ± 0.8	275.6 ± 6.7
52100 steel	5.2 ± 0.3	234.3 ± 3.9

TABLE V

Material	**Wear rate of counterbody [mm^3/N/m]**	**Wear rate of material [mm^3/N/m]**
Cr diffusion layer	2×10^{-6}	2×10^{-5}
52100 steel	5×10^{-7}	6×10^{-4}

[0047] With the AISI 52100 steel material as a substrate, surface hardness is increased four-fold by the application of the chromium diffusion layer as illustrated in Table IV. Table V indicates the wear rate of the 52100 steel substrate against a 52100 steel counterbody is decreased by an order of magnitude with the application of a chromium diffusion coating to the substrate.

[0048] In summary, this example illustrates that a robust process has been created that enables the creation of a chromium diffusion layer on an AISI 4140 steel or AISI 52100 steel substrate material. Moreover, this example shows that the chromium diffusion coating significantly increases the hardness of the treated substrate surface and reduces the wear rate of the treated substrate surface.

[0049] It should be appreciated that various other modifications and variations to the preferred embodiments can be made within the spirit and scope of the invention. Therefore, the invention should not be limited to the described embodiments. To ascertain the full scope of the invention, the following claims should be referenced.

CLAIMS

What is claimed is:

1. A method of forming a wear-resistant coating on an article using pack cementation, the method comprising:

providing a ferrous substrate material;

packing the ferrous substrate material in a powder comprising metal to be transferred to the substrate material;

reacting the metal to be transferred to the ferrous substrate material with a halide salt to form a metal-halide vapor species;

contacting the metal-halide vapor species with the ferrous substrate material, thereby transferring the metal to the ferrous substrate material; and

diffusing the metal into the ferrous substrate material, thereby forming the wear-resistant coating on the ferrous substrate material.

2. The method of claim 1, wherein the wear-resistant coating realizes a reduction in sliding wear rate compared to the ferrous substrate material prior to transfer of the metal into the ferrous substrate material.

3. The method of claim 1, wherein the metal transferred to the ferrous substrate material is chromium.

4. The method of claim 3, wherein the halide salt is NH_4Cl and the steps of reacting the metal to be transferred to the ferrous substrate material with a halide salt to form a metal-halide vapor species, contacting the metal-halide vapor species with the ferrous substrate material, and diffusing the metal into

the ferrous substrate material occurs in a range of 800°C to 1000°C for approximately 16 hours.

4. The method of claim 3, wherein the halide salt is NaF and the steps of reacting the metal to be transferred to the ferrous substrate material with a halide salt to form a metal-halide vapor species, contacting the metal-halide vapor species with the ferrous substrate material, and diffusing the metal into the ferrous substrate material occurs in a range of 800°C to 1000°C for approximately 16 hours.

5. The method of claim 3, wherein the wear-resistant coating of the ferrous metal substrate is a chromium diffusion layer.

6. The method of claim 3, wherein a thickness of the wear-resistant coating is in a range of 10 µm to 20 µm.

7. The method of claim 3, wherein diffusing the chromium into the ferrous substrate material occurs in a temperature range of 600°C to 1200°C.

8. The method of claim 1, wherein the metal reacts with the substrate material to form an intermetallic phase.

9. The method of claim 1, wherein a chemical diffusion zone is formed which bonds the ferrous substrate material to the wear-resistant coating.

10. The method of claim 1, wherein the metal transferred to the ferrous substrate includes at least one of silicon, chromium, aluminum, carbon or boron and

the halide salt includes at least one of NaF, NH_4Cl, MgF_2, and CuF_2.

11. The method of claim 1, wherein the ferrous substrate material is a member selected from the group consisting of AISI 4140 steel and AISI 52100 steel.

12. The method of claim 11, wherein the wear-resistant coating provides increased hardness and improved wear resistance in comparison to the ferrous substrate material without the wear-resistant coating.

13. The method of claim 1, wherein the wear-resistant coating is formed on a surface of the article that is a sliding contact surface during use of the article.

14. An article with a wear-resistant coating formed thereon, the article comprising a ferrous substrate material having a metal diffused into the ferrous substrate material to form a wear-resistant coating.

15. The article of claim 14, wherein the metal diffused in the ferrous substrate material is chromium.

16. The article of claim 14, further comprising an intermetallic phase formed between the metal and the substrate material.

17. The article of claim 14, further comprising a chemical diffusion zone bonding the substrate material to the wear-resistant coating.

18. The article of claim 14, wherein the article is a bushing.

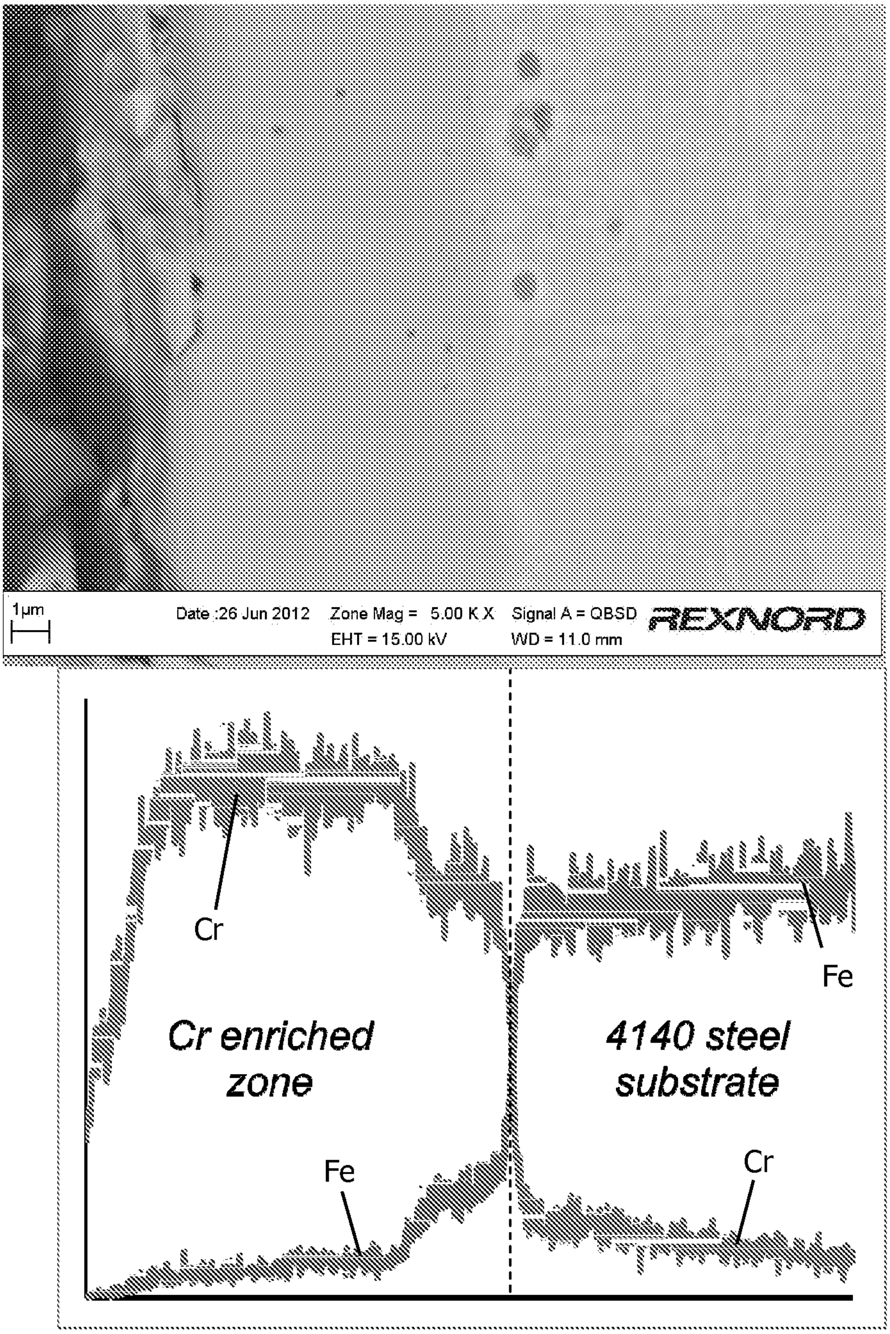
19. The article of claim 14, wherein the article is a race of a bearing.

20. The article of claim 14, wherein the article is a hinge pin for connecting links of a conveying surface.

21. The article of claim 14, wherein a thickness of the wear-resistant coating is in a range of 10 µm to 20 µm.

22. The article of claim 14, wherein the ferrous substrate material is a member selected from the group consisting of AISI 4140 steel and AISI 52100 steel and the metal diffused in the ferrous substrate material is chromium.

23. The article of claim 14, wherein the wear-resistant coating is formed on a surface of the article that is a sliding contact surface during use of the article.


1µm
Date :26 Jun 2012
Zone Mag = 5.00 K X
EHT = 15.00 kV
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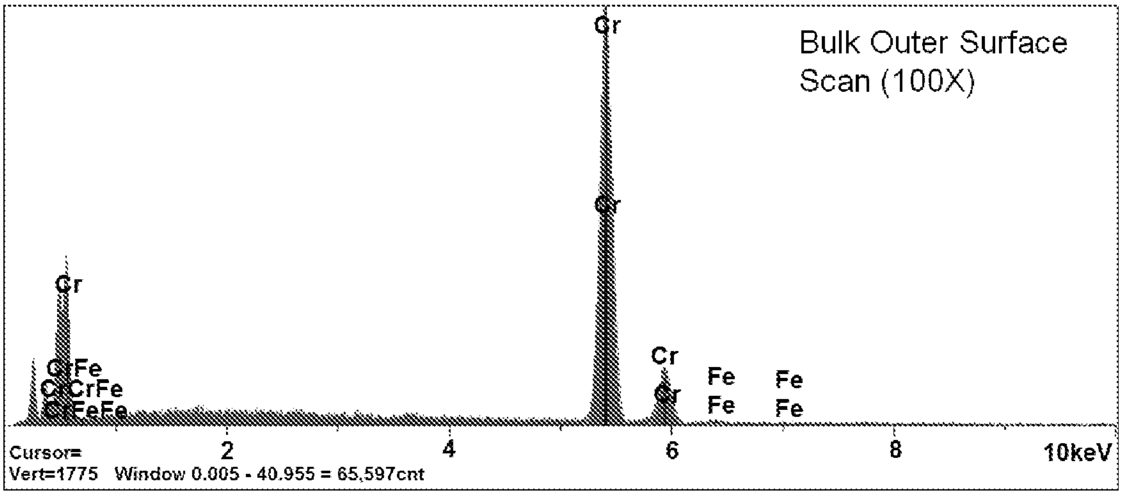
REXNORD
Cr
Fe
Cr enriched zone
4140 steel substrate
Fe
Cr

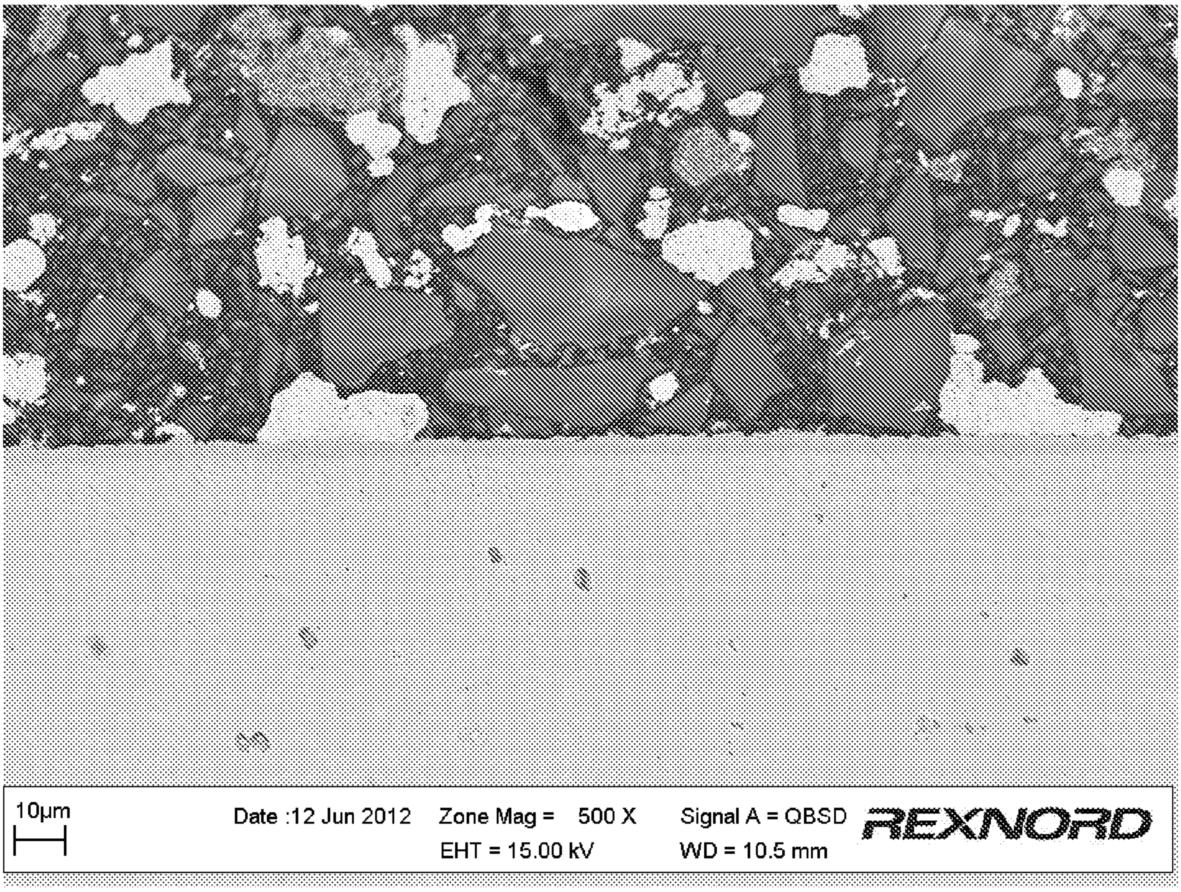
FIG. 1



Elt.	Line	Intensity (c/s)	Conc	Units	Error 2-sig	MDL 3-sig	
Cr	Ka	774.05	98.994	wt.%	1.319	0.345	
Fe	Ka	4.81	1.006	wt.%	0.336	0.446	
			100.000	wt.%			Total

kV 25.0
Takeoff Angle 35.0°
Elapsed Lifetime 30.0

FIG. 2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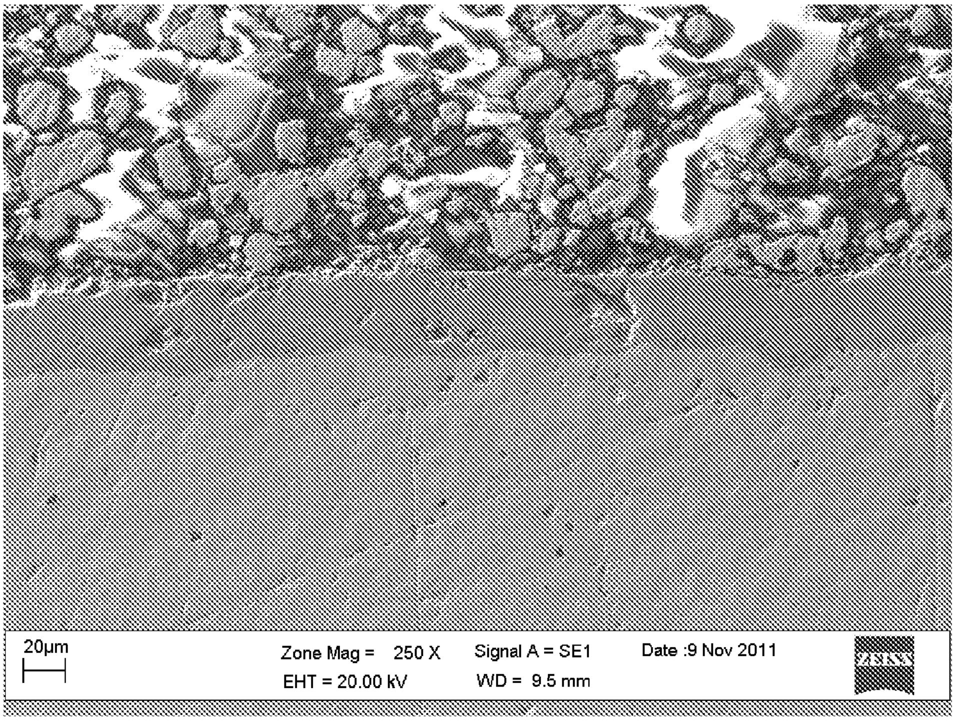
REXNORD

FIG. 3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EHT = 20.00 kV
Signal A = SE1
WD = 9.5 mm
Date :9 Nov 2011
ZEISS

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/055074

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C10/42 C23C10/50 C23C10/54 C23C10/56
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 3 083 122 A (GEORGE WEATHERLEY ERIC ET AL) 26 March 1963 (1963-03-26) column 1, line 10 - line 15 column 2, line 13 - line 25 column 3, line 56 - line 63; claims 1-28 -----	1-23
X	GB 727 567 A (METAL GAS COMPANY LTD) 6 April 1955 (1955-04-06) page 4, line 56 - line 100; claims 1-11 -----	1-23
X	FR 1 146 767 A (NAT D ETUDES & DE RECH S AERON) 14 November 1957 (1957-11-14) claim 1; examples 2,3,5 -----	1-23
X	FR 1 237 713 A (ONERA) 5 August 1960 (1960-08-05) claim 1; example 5 ----- -/--	1-23

☒ 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

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"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

"&" document member of the same patent family

Date of the actual completion of the international search
18 April 2013

Date of mailing of the international search report
25/04/2013

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INTERNATIONAL SEARCH REPORT

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