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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
25 April 2013 (25.04.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/056847 A1

(51) International Patent Classification:
C21D 1/68 (2006.01) *C09D 201/10* (2006.01)
C23C 18/02 (2006.01) *C09D 175/04* (2006.01)
C09D 7/12 (2006.01) *C09D 183/04* (2006.01)
C09D 5/10 (2006.01)

(21) International Application Number:
PCT/EP2012/004384

(22) International Filing Date:
19 October 2012 (19.10.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11008421.7 19 October 2011 (19.10.2011) EP

(71) Applicant: **TATA STEEL UK LIMITED** [GB/GB]; 30 Millbank, London SW1P 4WY (GB).

(72) Inventors: **GORDON, Douglas Jesus Figueroa**; Tata Steel Nederland Technology BV, Group Intellectual Property Services 3G37, P.O. Box 10000, NL-1970 CA Ijmuiden (NL). **HARDING, Tim**; Tata Steel Nederland Technology BV, Group Intellectual Property Services 3G37, P.O. Box 10000, NL-1970 CA Ijmuiden (NL). **BÖHM, Sivasambu**; Tata Steel Nederland Technology BV, Group Intellectual Property Services 3G37, P.O. Box 10000, NL-1970 CA Ijmuiden (NL). **LI, Wu**; Tata Steel Nederland Technology BV, Group Intellectual Property Services 3G37, P.O. Box 10000, NL-1970 CA Ijmuiden (NL). **WEIRMAN, Chris**; Tata Steel Nederland Technology BV, Group Intellectual Property Services 3G37, P.O. Box 10000, NL-1970 CA Ijmuiden (NL).

(74) Agent: **KRUIT, Jan**; Tata Steel Nederland Technology BV, Group Intellectual Property Services - 3G37, P.O. Box 10000, NL-1970 Ca Ijmuiden (NL).

(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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, 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, 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, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,

[Continued on next page]

(54) Title: ANTI-SCALE AND ANTI-CORROSION HYBRID COATINGS FOR STEEL SUBSTRATES

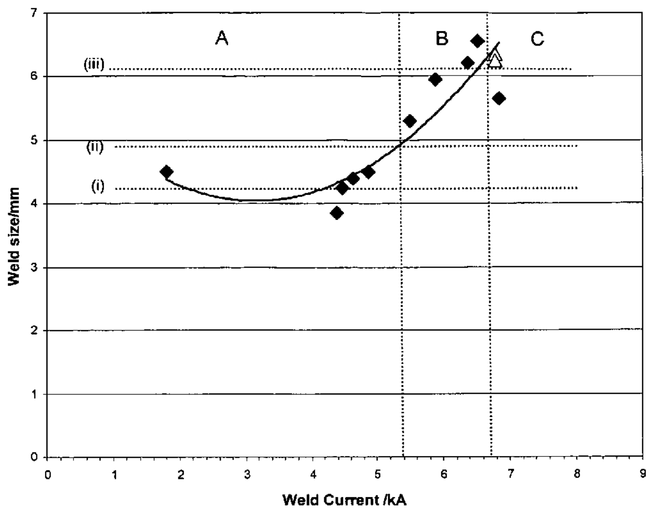

Fig.1

(57) Abstract: Method of producing a coated steel substrate suitable for hot-forming or other high temperature applications, which comprises the steps of: (i) providing a steel substrate; (ii) preparing a coating mixture comprising a curable organic component as a first binder, a curable inorganic component as a second binder, a cross- linking component to chemically cross-link the curable organic component and the curable inorganic component, and a metal or metal alloy particle having an aluminium content of at least 50 wt% and a balance of 50 wt% or less of a non-aluminium metal; (iii) applying the mixture on the steel substrate; (iv) curing the mixture so as to produce a dense network structure of the coating on the steel substrate.

WO 2013/056847 A1

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, ML, MR, NE, SN, TD, TG).

Published:

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

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

ANTI-SCALE AND ANTI-CORROSION HYBRID COATINGS FOR STEEL SUBSTRATES

FIELD OF THE INVENTION

The present invention relates to a coated steel substrate and to a method for manufacturing the same. The invention also relates to a method of hot-forming or cold-forming the coated steel substrate to produce hot-formed and cold-formed articles. The invention further relates to the use of the hot-formed and cold-formed articles in the manufacture of automotive vehicles.

BACKGROUND OF THE INVENTION

The use of high strength steels for structural parts in automobiles has increased in recent years due to the high mechanical properties of such steels. By hot-forming, the manufacturer is able to produce parts having superior shape complexity and strength.

Hot-forming is usually performed by providing a steel sheet blank, heating the blank in a heating furnace to a temperature between 800 and 1200°C, placing the heated blank in a hot forming press, forming the blank into a part in the hot forming press and hardening the hot formed part.

High temperature oxidation at the steel surface is a common problem which reduces the spot weldability of the part and adversely affects the appearance of the part after paint baking. Uncoated blanks are therefore hot-formed under inert conditions to reduce oxidation and decarburisation of the steel during the heating and hot-forming of the blank. Nevertheless, when the blank is transferred from the heating furnace to the hot-forming press, oxidation of the blank can occur meaning the part must be de-scaled after hot-forming.

In an attempt to minimise oxidation and decarburisation still further, steel sheets are often provided with protective metallic coatings. Common protective coatings are based on zinc or zinc alloys. Zinc or zinc alloy coatings rely on the formation of a diffusion layer to prevent against high temperature oxidation, which diffusion layer comprises at least oxides of zinc. Although the diffusion layer provides protection against high temperature oxidation of the substrate and ensures good adhesion between the metal coating and the substrate, the thin oxide layer has a negative impact on spot weldability, and therefore an additional process step to remove the oxide layer is required.

An object of the invention is to provide a coated steel substrate having improved weldability properties, particularly with respect to zinc or zinc alloy coated steel substrates, after hot-forming or other high temperature processes.

Another object of the invention is to provide a coated steel substrate, which after hot-forming or when used in high temperature service conditions, is resistant to corrosion.

A further object of the invention is provide a coated steel substrate, which after hot-forming does not require an additional process step to remove oxide scales from the substrate surface.

DESCRIPTION OF THE INVENTION

The first aspect of the invention relates to a method of producing a coated steel substrate suitable for hot-forming or other high temperature applications, which comprises the steps of:

(i) providing a steel substrate;
(ii) preparing a coating mixture comprising a curable organic component as a first binder, a curable inorganic component as a second binder, a cross-linking component to chemically cross-link the curable organic component and the curable inorganic component, and a metal or metal alloy particle having an aluminium content of at least 50 wt% and a balance of 50 wt% or less of a non-aluminium metal;
(iii) applying the mixture on the steel substrate;
(iv) curing the mixture so as to produce a dense hybrid network structure of the coating on the steel substrate.

The coated steel substrate is suitable for use in hot-forming and in high temperature service conditions where substrates experience temperatures of up to 950°C and 550°C respectively. By providing the cross-linking component in the coating mixture the curable organic component and the curable inorganic component form an organic-inorganic hybrid network upon curing. The inventors have found that the scratch resistance of the cured coating comprising the organic-inorganic hybrid network is improved to an extent that the coating can withstand the handling and blanking operations prior to hot-forming.

During the heat treatment that precedes hot-forming the organic-inorganic hybrid network thermally degrades, leaving behind a sintered coating comprising the inorganic component and the metal or metal alloy particle. Thermal degradation of the organic component and the cross-linking component typically occurs at temperatures above 250°C, although this depends of the thermal properties of the said components.

By cross-linking the organic curable component with the curable inorganic component the inventors have found that the conductivity of the sintered coating comprising the inorganic component and the metal or metal alloy particle can be increased. In this connection the metal particle binding properties of the organic-inorganic hybrid network are greater than that of other coatings which make use of mixed organic/inorganic binders without cross-linking or modified silanes. This unexpected improvement in binding properties means that the content of the curable inorganic component in the coating mixture can be reduced relative to coatings comprising modified silanes or mixed organic/inorganic binders.. This has the advantage that the content of the insulating inorganic component in the sintered coating will also be reduced and as a consequence a much higher coating conductivity is obtained.

The inventors have also found that coating mixtures comprising a metal particle and/or a metal alloy particle having an aluminium content greater than 50 weight% were particularly effective in reducing the formation of oxide scales at the steel substrate surface during/after the heat treatment and/or hot-forming or during high temperature service conditions up to 550°C.

In a preferred embodiment the non-aluminium metal comprises zinc, magnesium, nickel, copper, tin or mixtures thereof. Zinc and magnesium oxidise in preference to iron and are therefore suitable to act as a sacrificial anode if the intermetallic layer is damaged. Coating mixtures which do not comprise magnesium and/or zinc as the non-aluminium metal will exhibit anti-scale and barrier protection properties only. Magnesium also limits the amount of zinc that is evaporated when the coated steel substrates are used in hot-forming. A preferred zinc and/or magnesium content in the form of metal particles or as a metal alloy is between 1 and 30 wt%, more preferably between 10 and 20 wt%, since the use of more than 30 wt% of magnesium and/or zinc at the expense of aluminium will reduce the oxidation protection properties of the coating. If nickel, copper or tin are used as the non-aluminium metal then the coating mixture should comprise less than 1 wt% of these metals to avoid reduced interfacial bonding between the coating and the substrate. Preferably the coating mixture comprises 10-30 wt% metal or metal alloy particle, preferably 10-20 wt%.

In a preferred embodiment the curable organic component comprises polyurethanes polyesters, acrylates and resins of epoxies or melamin. These curable organic components comprise reactive groups which react with the cross-linking component and/or directly with the curable inorganic component to form the organic-inorganic hybrid network. Preferably the coating mixture comprises 4-20 wt%, more preferably 4-10 wt% of the curable organic component.

In a preferred embodiment the curable inorganic component comprises a hydrolysable silane or derivative thereof. The hydrolysable silanes comprise hydroxyl, epoxy, acrylate and amino functional groups which react with the cross-linking component and/or directly with the curable organic component. Preferably the coating mixture comprises 10-30 wt%, more preferably 10-20 wt% of the curable inorganic component.

In a preferred embodiment of the invention the cross-linking component comprises melamin and isocyanate. These cross-linking components have reactive functional groups which react with the curable organic component and the curable inorganic component upon curing.

Preferably the coating mixture comprises 1-10 wt%, more preferably 2-7 wt% of the cross-linking component

In a preferred embodiment the steel substrate is a hot-formable steel substrate, preferably containing in weight %: 0.15 - 0.5 C, 0.5 - 3.0 Mn, 0.1 - 2.5 Si, < 0.1 Al, < 1.0 Cr, < 0.2 Ti, < 0.1 P, < 0.05 S, < 0.08 B, < 0,1 V, < 0.5 Mo, < 0.003 ppm Ca, optionally < 0.1 Nb, unavoidable impurities, the remainder being iron. Steel substrates having the above composition are particularly suitable for hot-forming, cold-forming and for use in high temperature service conditions. Preferred steel substrates comprise advanced high strength steel, ultra high strength steels and boron steels.

In a preferred embodiment the aluminium and/or non-aluminium particle or alloy particle is encapsulated with an encapsulating component prior to the step of preparing the coating mixture. The encapsulation of aluminium and/or the non-aluminium particle such as zinc and magnesium may be necessary to prevent said metals from reacting with water during paint production or storage. Preferred encapsulating components comprise silica, titania, acrylates or derivatives thereof.

In a preferred embodiment the coating mixture additionally comprises a non-metallic conductive component. Preferably the non-metallic conductive component comprises ferrophos (Fe_2P) pigments, micaceous iron oxide, carbon nanotubes, titanium nitride, titanium carbide and boron nitride. Preferably the coating mixture comprises ≤ 5 wt% of the non-metallic conductive component. A non-metallic conductive component content of 1-4 wt% is particularly preferred.

Ferrophos pigments consist essentially of Fe_2P although trace amounts of silicon dioxide are also present. These pigments are electrically and thermally conductive and chemically inert under standard atmospheric conditions. Ferrophos has a melting point of 1320°C making is particularly suitable as a conductive component for use in high temperature applications.

Micaceous iron oxide (MIO) consists essentially of Fe_2O_3 and differs from other well known iron oxide pigments. Advantageously, micaceous iron oxide is insoluble in water, organic solvents and alkalis and is only soluble in strong acids which are heated to elevated temperatures. MIO has a melting point in excess of 1500°C and is particularly suitable for use in high temperature applications such as hot-forming. When MIO is added to the coating mixture of the invention MIO thin flakes having a thickness between 1-7 μm align substantially parallel to the substrate surface to produce a protective barrier of overlapping flakes. The addition of 1-4 wt% of MIO to the coating mixture is particularly effective in improving the barrier properties of the coating.

Preferably the coating mixture comprises organophosphates since the inclusion of such compounds further extends the lifetime of the coating and the coated steel substrate.

In preferred embodiment the coating mixture comprises 4-20 wt% curable organic component, 10-30 wt% curable inorganic component, 1-10% cross-linking component, 10-30 wt% metal or metal alloy particle and 35-55 wt% solvent, preferably the coating mixture comprises 4-10 wt% curable organic component, 10-20 wt% curable inorganic component, 2-7 wt% cross-linking component, 10-20% metal or metal alloy particle and 35-55 wt% solvent

In a preferred embodiment of the invention the solvent comprises water or a mixture of water and an organic solvent. The use of water or a water based solution as the solvent avoid and reduces respectively, the issues associated with the handling and disposal of organic solvents.

The second aspect of the invention relates to the coated steel substrate produced according to the first aspect of the invention. Preferably the coating of the coated steel substrate has a dry film thickness of 3-30 μm. The inventors have found that coatings having dry film thicknesses below 3 μm did not offer sufficient oxidation protection, whereas a dry film thickness above 30 μm meant that the coatings were prone to delamination. A dry film thickness of 5-10 μm is preferred so that a good balance between coating integrity, flexibility and oxidation protection is obtained.

The third aspect of the invention relates to a method of producing a hot-formed article comprising the steps of:

i. providing the coated steel substrate according to the second aspect of the invention;
ii. heating the coated steel substrate to a temperature above the Ac1 temperature to austenise the steel;
iii. hot-forming the coated steel substrate in a hot-forming apparatus comprising a die;
iv. quenching the formed coated steel substrate in the die to form the hot-formed article.

When the coated steel substrate is used in hot-forming, the substrate is heated in a heating furnace to a temperature above Ac1 temperature to austenise the steel substrate. The austenised substrate is then transferred to a hot-forming apparatus where the coated substrate is formed and quenched to obtain a hot-formed part having a high tensile strength. A diffusion layer is formed during the heat treatment (>600°C) that precedes hot-forming, which reduces oxidation at the steel substrate surface. The diffusion layer comprises iron from the steel and one or more metals from the metal or metal alloy particles. The substantial absence of oxide scales means that the hot-formed article can be easily painted after hot-forming since no additional step to remove oxide scales is required.

As the steel substrate approaches the austenisation temperature an intermetallic layer is formed on the diffusion layer between 700 and 950°C. This intermetallic layer comprises the metals of the metal or metal alloy particles, which melt to form a continuous layer. The presence of the intermetallic layer affords the steel substrate improved corrosion protection after hot-forming because the metals of the intermetallic layer act as a sacrificial anode if the intermetallic layer is damaged. When the inorganic component is a silane, the intermetallic layer may additionally comprise silica particles which are produced when silanes are heated at elevated temperatures.

The fourth aspect of the invention relates to the hot-formed article produced according to the third aspect of the invention wherein the electrical resistance of the hot-formed article is less than 5 mOhm, preferably between 0.1 and 2 mOhm. This has the advantage that the hot-formed article is very suitable for spot welding because and no further process is required to increase the conductivity of the hot-formed article.

The fifth aspect of the invention relates to a method for producing a cold-formed article which comprises the steps of:

i. providing the coated steel substrate according to the second aspect of the invention;
ii. cold-forming the coated steel substrate.

When the cold-formed article is used in high temperature service conditions up to 550°C, for instance in exhausts, a sintered coating comprising the inorganic component and the metal or metal alloy particle is produced due to the organic component and the cross-linking component thermally degrading at temperatures above 250°C.

The sixth aspect of the invention relates to the cold-formed article produced according to the method of the fourth aspect of the invention. The sintered coating of the cold-formed article acts as a protective barrier whereas the metal or metal alloy particles contribute to reducing the formation of oxide scales at the steel substrate surface. The oxidation protection performance of the coated steel substrate is comparable to that of aluminised coatings that are often used in high temperature service conditions. Advantageously the comparable properties are obtained at reduced coating thicknesses relative to the aluminised coatings. Sacrificial corrosion protection is conferred to the steel substrate when metals which corrode in preference to iron are used as the non-aluminum metal.

The seventh aspect of the invention relates to the use of the hot-formed article according to the fourth aspect of the invention and/or the cold-formed article of the sixth aspect of the invention in the manufacture of automotive vehicles.

EXAMPLES

The invention will now be further explained by the following non-limitative examples.

Example 1: Preparation of a coating mixture

Coating mixture (1)

100g of aluminium flake paste (Eckart Stapa ® Hydrolan 1515nl) was added to a mixing vessel. 5g of DisperBYK 192 and 100g of water were then added under moderate agitation (500-800 rpm). The coating mixture was completed by the addition of 208g of Hydrosil™ 2926 water-based functional silane, 62g polyurethane dispersion Hybridur (Air Product), 29g cross linker Cymel 328, 1.2g of BYK348 and 0.45g of BYK024.

Example 2: Coating application

Coating mixture (1) was applied on a boron steel strip by spray coating to provide a uniform coating thereon. The coated steel strip was then cured using induction or infrared heating to cure the coating mixture.

Experiments

Spot weldability

After a heat treatment under N_2 purging at 920 °C the coated steel substrate was subjected to a spot-welding test (BS1140) to determine the welding range. Figure 1 shows the results of the spot welding test for coated boron steel strip provided with coating mixture (1). The measured electrical resistance was below 1 mOhm and a welding range of 1.4 kA was obtained. Region B shows the useful spot welding range, whereas region C is the region in which splash occurs between the steel sheets. The dotted lines (i), (ii) and (iii) correspond to a weld size of 3, 4 and 5 $\sqrt{t}$ respectively where t is the steel substrate thickness (t =1.45 mm).

Scratch resistance

European standard BS EN 13523-4:2001 was used to determine the pencil hardness of the cured coating comprising the inorganic component and the metal or metal alloy particle. Pencil hardness may be defined as the resistance of the surface of the cured coating to marking or other defects caused by the action of pencil pushed against the surface, the pencil having a specified dimension, shape and hardness of lead. After curing, steel substrates that were coated with coating (1) exhibited a pencil hardness value of 4H-6H.

CLAIMS

1. Method of producing a coated steel substrate suitable for hot-forming or other high temperature applications, which comprises the steps of:
   (i) providing a steel substrate;
   (ii) preparing a coating mixture comprising a curable organic component as a first binder, a curable inorganic component as a second binder, a cross-linking component to chemically cross-link the curable organic component and the curable inorganic component, and a metal or metal alloy particle having an aluminium content of at least 50 wt% and a balance of 50 wt% or less of a non-aluminium metal;
   (iii) applying the coating mixture on the steel substrate;
   (iv) curing the mixture so as to produce a dense hybrid network structure of the coating on the steel substrate.

2. Method according to claim 1, wherein the non-aluminium metal comprises zinc, magnesium, nickel, copper, tin or mixtures thereof.

3. Method according to claim 1 or claim 2, wherein the curable organic component comprises polyurethanes polyester, epoxy resin, acrylates and melamin resins.

4. Method according to any one of the preceding claims wherein the curable inorganic component comprises a hydrolysable silane or derivative thereof, preferably epoxy or amino hydrolysable silanes.

5. Method according to any one of the preceding claims wherein the cross-linking component comprises melamin and isocyanate.

6. Method according to any one of the preceding claims, wherein the steel substrate is a hot-formable steel substrate, preferably containing in weight %: 0.15 - 0.5 C, 0.5 - 3.0 Mn, 0.1 - 2.5 Si, < 0.1 Al, < 1.0 Cr, < 0.2 Ti, < 0.1 P, < 0.05 S, < 0.08 B, < 0,1 V, < 0.5 Mo, < 0.003 ppm Ca, optionally < 0.1 Nb, unavoidable impurities, the remainder being iron.

7. Method according to any one of the preceding claims, wherein the aluminium and/or non-aluminium particle or alloy particle is encapsulated with an encapsulating component prior to the step of preparing the coating mixture.

8. Method according to any one of the preceding claims, wherein the coating mixture additionally comprises a non-metallic conductive component.

9. Method according to any one of the preceding claims wherein, the coating mixture comprises 4-20% curable organic component, 10-30% curable inorganic component, 1-10 cross-linking component and 10-30 wt% metal or metal alloy particle.

10. Method according to any one of the preceding claims wherein the solvent comprises water or a mixture of water and an organic solvent.

11. Coated steel substrate produced according to the method of any one of claims 1-10, preferably having a dry film thickness of 3-30 μm.

12. Method of producing a hot-formed article comprising the steps of:
   i. providing the coated steel substrate according to claim 11;
   ii. heating the coated steel substrate to a temperature above the Ac1 temperature to austenise the steel;
   iii. hot-forming the coated steel substrate in a hot-forming apparatus comprising a die;
   iv. quenching the formed coated steel substrate in the die to form the hot-formed article.

13. Hot-formed article produced according to the method of claim 12 wherein the electrical resistance of the hot-formed article is less than 5 mOhm, preferably between 0.1 and 2 mOhm.

14. Method of producing a cold-formed article which comprises the steps of:
   i. providing the coated steel substrate according to claim 11;
   ii. cold-forming the coated steel substrate.

15. Cold-formed article produced according to the method of claim 14.

16. Use of the hot-formed article according to claim 13 and/or the cold-formed article according to claim 15 in the manufacture of automotive vehicles.

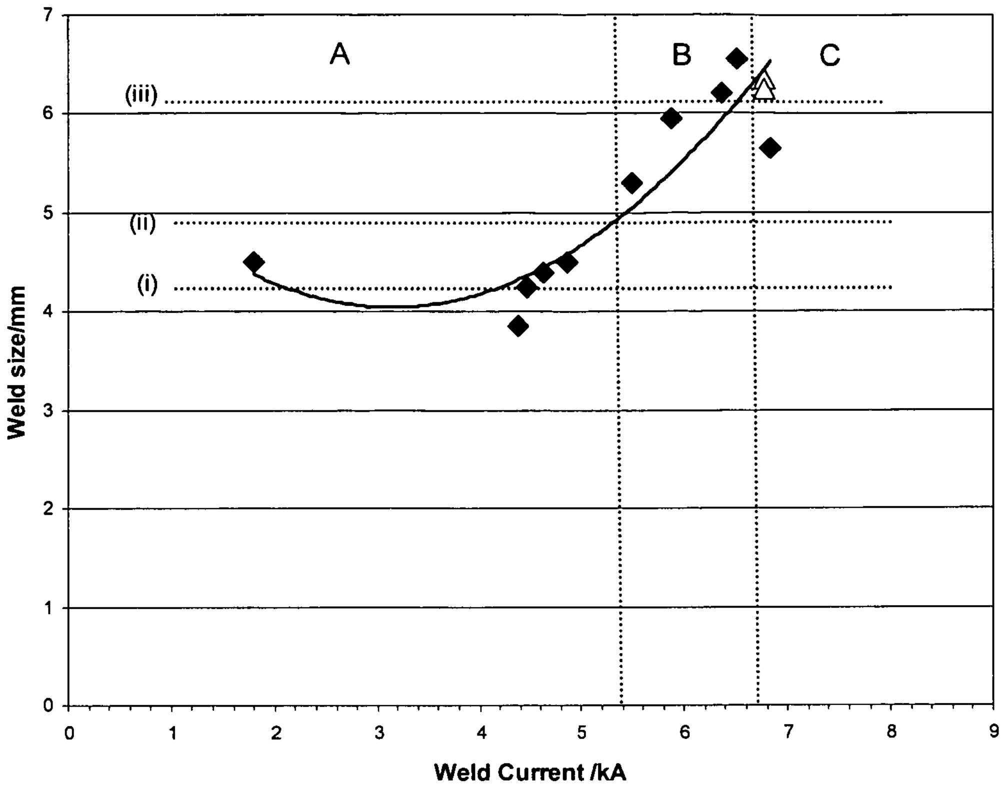

Fig.1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/004384

A. CLASSIFICATION OF SUBJECT MATTER
INV. C21D1/68 C23C18/02 C09D7/12 C09D5/10 C09D201/10
C09D175/04 C09D183/04
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)
C21D C23C C09D

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 Y	US 4 250 074 A (FOSCANTE RAYMOND E [US] ET AL) 10 February 1981 (1981-02-10) column 3, line 44 - line 57 column 7, line 58 - line 65 column 10, line 41 - line 55 claims 1,2,11-13,23,43	1,3,4,6,10,11 7,8,12-16
X	WO 2007/067203 A1 (GEN ELECTRIC [US]; LEJEUNE ALAIN [FR]; GENTIL YVES [FR]) 14 June 2007 (2007-06-14) claims 1,10-12, 16,21,23-27,31,33 page 2, paragraph 3 page 11, paragraph 3 page 18, paragraph 1 - paragraph 2	1-6,9-11
X	EP 0 385 880 A2 (SAVIN RONALD RICHARD [US]) 5 September 1990 (1990-09-05) claims 1-3, 5, 11,15	1,3-6,9-11

-/--

[X] Further documents are listed in the continuation of Box C.

[X] 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

"E" earlier application or patent but published on or after the international filing date

"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)

"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

"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

"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

"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	Date of mailing of the international search report
8 March 2013	18/03/2013

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

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/004384

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	WO 2011/069663 A2 (TATA STEEL UK LTD [GB]; GORDON DOUGLAS JESUS FIGUEROA [NL]; HARDING TI) 16 June 2011 (2011-06-16) claims 1-4,7-9,11,12,14; examples 1,5 -----	7,8, 12-16 1,2,5,10
A	WO 2010/069588 A1 (CORUS STAAL BV [NL]; HENSEN GUIDO CORNELIS [NL]; VERLOOP WICO CORNELIS) 24 June 2010 (2010-06-24) claims 9-13 -----	6
A	US 2010/159144 A1 (STANDKE BURKHARD [DE] ET AL) 24 June 2010 (2010-06-24) claim 1 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/004384

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4250074 A	10-02-1981	KR 830001473 A	30-07-1983
		US 4250074 A	10-02-1981
WO 2007067203 A1	14-06-2007	BR PI0619555 A2	04-10-2011
		CA 2633135 A1	14-06-2007
		CN 101365763 A	11-02-2009
		EP 1971658 A1	24-09-2008
		JP 2009518503 A	07-05-2009
		KR 20080078824 A	28-08-2008
		US 2006225612 A1	12-10-2006
		WO 2007067203 A1	14-06-2007
EP 0385880 A2	05-09-1990	CA 2011387 A1	03-09-1990
		EP 0385880 A2	05-09-1990
WO 2011069663 A2	16-06-2011	CN 102652157 A	29-08-2012
		EP 2510061 A2	17-10-2012
		WO 2011069663 A2	16-06-2011
WO 2010069588 A1	24-06-2010	CA 2746212 A1	24-06-2010
		CN 102257166 A	23-11-2011
		EP 2379756 A1	26-10-2011
		JP 2012512747 A	07-06-2012
		KR 20110118621 A	31-10-2011
		US 2011236719 A1	29-09-2011
		WO 2010069588 A1	24-06-2010
US 2010159144 A1	24-06-2010	AT 461252 T	15-04-2010
		BR PI0621243 A2	06-12-2011
		CN 101007303 A	01-08-2007
		DE 102006003956 A1	02-08-2007
		EP 1976946 A2	08-10-2008
		JP 2009524512 A	02-07-2009
		KR 20080089458 A	06-10-2008
		US 2010159144 A1	24-06-2010
		WO 2007085339 A2	02-08-2007