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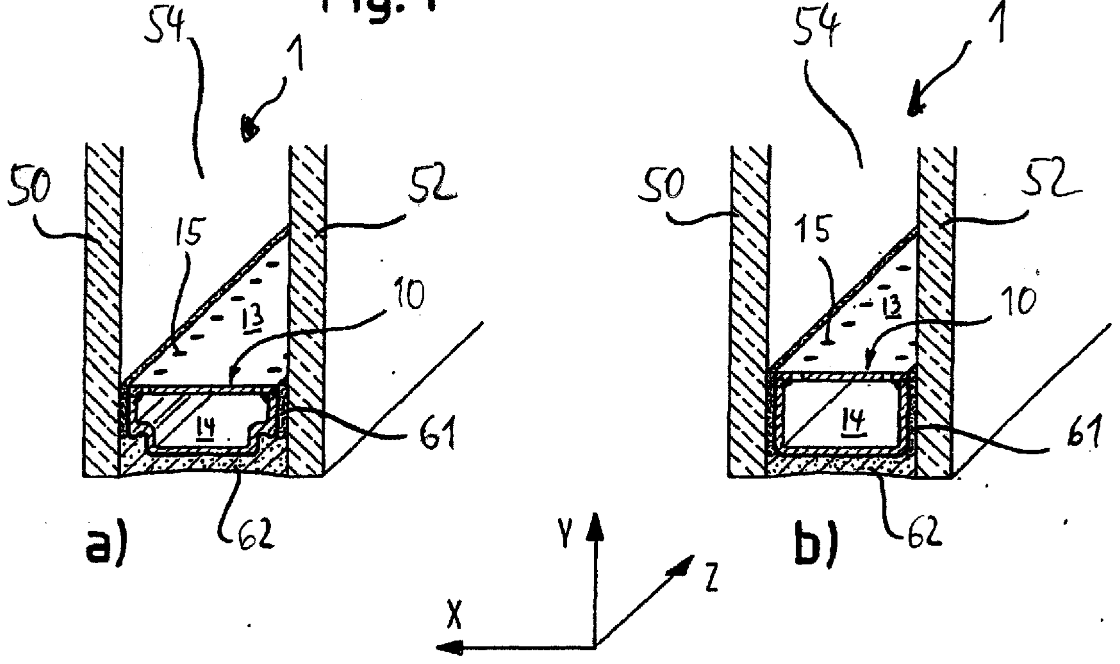
(54) Spacer for insulating glazing units having a metal layer with enhanced adhesion properties

(57) A spacer for an insulating glass unit (1) with at least two glass panes (50, 52), comprising a metallic layer (30), wherein the metallic layer (30) has a basic layer (30b) and at least one oxide layer (30a), and the basic layer (30b) is made of stainless steel, and the oxide layer (30a) is provided on the basic layer by oxidation, the oxide layer (30a) provides improved adhesion properties in comparison to the basic layer.

Fig. 1



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Description

[0001] The present disclosure relates to spacers for Insulating Glazing Units (IGUs).

[0002] The process of manufacturing IGUs is well known and established. The known IGUs may be formed of at least two glass panes being connected with each other via a spacer thus forming an interspace between the panes. Specifically, the spacer may be connected to each of the glass panes by at least one kind of sealant. The spacer itself may be formed as a hollow profile preferably made of a synthetic material and having a metallic layer, which forms at least parts of the outer surface of the spacer. The metallic layer may be a diffusion barrier layer for reducing/avoiding diffusion through the spacer and/or a reinforcement layer for reinforcing the spacer. The spacer may have different shapes. For example, a basically triangular / pyramidal shape or rectangular shape is formed. The chamber formed by the hollow profile may be filled with desiccant and is normally communicated to the interspace formed between the panes.

[0003] Accordingly, the glass panes of the IGU may be connected and supported on each other via a path formed by sealant-spacer-sealant. Often, a primary sealant and a secondary sealant is used. The primary sealant may be provided between the side surfaces of the spacer, which face the glass panes, and the surfaces of the glass panes and may be used for gas insulation. The secondary sealant may be provided in the outside groove (facing away from the interspace between the glass panes), which is formed by the glass panes and the spacer, and may be used for adhesive connection between glass panes and the glass panes and the spacer. The primary sealant may be used for the connection between side walls of the spacer facing the glass panes, respectively, while the secondary sealant may be present in the outside groove formed by the glass panes and the spacer.

[0004] For the mechanically stability of the IGU, it is important that the adhesion properties of the sealants to the spacer are good. As the sealants should adhere to the metallic layer, which forms at least partly the surface of the side walls (facing a glass pane, respectively) and/or of the outer wall (opposite to the interspace between the panes) of the spacer, in particular, the adhesion properties of the metallic layer are important.

[0005] Examples for the above described spacers are described and disclosed in EP 1 017 923 B1, EP 1 529 920B1 and EP 1 797 271 B1.

[0006] It is an object of the invention to provide a spacer having enhanced adhesion properties allowing a good permanent adhesion between the glass panes and the spacer by the sealants.

[0007] This object is achieved by a spacer according to claim 1. Further developments are given in the dependent claims.

[0008] It has been found that the metallic layer made of a stainless steel having an increased amount of oxides and/or hydroxyl groups on its surface shows by far better adhesion to one or more sealants, in particular to the secondary sealant, than a "normal" stainless steel. Such an increased amount of oxides and/or hydroxyl groups may be created, for example, by further oxidizing the stainless steel material, for example, in a final annealing step or by chemical treatment. Oxidizing stainless steel materials in known in the art and oxidized stainless steel materials are available on the market. In this respect, it is noted that some of the stainless steel materials are produced without a specific oxidizing step but have already a certain thicker oxide layer due to the manufacturing process. Indeed, in general, commercially available stainless steel materials can be considered oxidized materials due to the passivation process which creates the hard, protective layer (mainly of Chrome oxides) which makes the steel "stainless"

[0009] In the following, the term **"oxide stainless steel"** refers to a stainless steel having an increased amount of oxides and hydroxyl groups on its surface in comparison to a "normal stainless steel". That is, the surface is oxidized.

[0010] "Normal stainless steel" refers to a commercially available stainless steel produced with standard settings.

[0011] In the same way, the term **"oxide spacer"** refers to a spacer having an external barrier layer made of "oxide stainless steel", such barrier being in contact with sealant materials.

[0012] The term "adhesion properties", as it is used here and in the following should be understood as the characteristics/properties of a surface to allow an adhesion/bonding of another material (here preferably sealant) to the surface.

[0013] Normally the adhesion properties are measured by so-called tension tests, in which the adhering force, adhering durability (time until the material detaches) and the type rupture, for example, are measured.

[0014] In one of these tests, two pieces of spacer are joined by means of a mass of (secondary) sealant (typically Polysulphide, Polyurethane or Silicon) which adheres to the respective outer stainless steel foils. A force is applied to the two spacer pieces in such a way that the two spacer pieces are moved away from each other. In this way, the mass of secondary sealant is under stress. The result is considered good if the force causing the break of the sample is over 10 daN and the rupture is cohesive, i.e. the fracture occurs in the mass of sealant.

[0015] This test is a tensile test as generally this term is considered in the art, especially in the field of applied mechanics, because an increasing force is applied to the sample till rupture of the sample itself.

[0016] The reference European standard for IGUs EN1279 proposes a different kind of test, called "tensile test" in which the durability is measured. It is described in Annex F of part 6 of EN1279. According to said standard, two length of spacer bar are placed in parallel 11.5 mm apart. The gap can be filled with (secondary) sealant by using a non-adhering plate on the opposite side. A defined load is applied to the test specimen by hanging weights on it. The result is considered to be good if the specimen lasts at least 10min before rupture.

[0017] The present invention improves at least one of these adhesion properties (e.g. the type of break, the force and the time until break) with respect to both of the above or other tests, for example.

[0018] The use of such oxide stainless steel for spacers has the following advantages:

- improvement of adhesion to sealants; this implies improved "reserve capacity" against pumping effects due to climatic changes; therefore , the integrity of IGUs is preserved for a longer time and consequently lifetime of IGUs is extended;
- due to better adhesion to secondary sealants, the mass of secondary sealant can be reduced; consequently, heat transfer through the composite edge of IGU is significantly reduced;
- less amount of secondary sealant means lower thickness of secondary sealant, which means that, ceteris paribus, the spacer can be placed closer to the edges of glass panes, therefore the path for heat is made longer and the overall heat transfer is reduced (spacer depth in the window system is higher). It is also possible to think keeping the heat transfer constant; in this case, the height of the legs of the window frame can be reduced of the same amount as the reduction of thickness of secondary sealant so that, consequently, the visible area through the glass of the window is larger (such trend being greatly appreciated by the market);
- because of improved adhesion, mechanical strength and lateral resistance of IGU are at the same level of current IGUs despite the use of less amount of sealant;
- different steel grades have different adhesion properties (example 1.4016, 1.4301, 1.4310, 1.4372). However, the use of an increased amount of hydroxyl groups / metal oxides is helpful for all steel grades;
- handling at customers is safer: indeed, impurities on the surface of stainless steel barrier of spacer can negatively affect bonding properties to secondary sealants; with oxide stainless steels, an increased "adhesion reserve" is available (thanks to increased amount of hydroxyl groups / metal oxides on surface) in case impurities lower the adhesion properties of steel.

[0019] One aspect of the present invention is a spacer for IGUs having an external stainless steel barrier foil which is in contact with secondary sealant, wherein the stainless steel foil has an increased amount of hydroxyl groups / metal oxides on its external surface in comparison to a normal stainless steel. Preferably the spacer according to this disclosure does not refer to seal members used at the boundary of vacuum glass.

[0020] Another aspect of the present invention is the use of a special class of stainless steels - having increased amount of hydroxyl groups / metal oxides on its surface in comparison to a normal stainless steel - as barrier foil for insulating spacers for IGUs.

[0021] Further features and usabilities follow from the description of exemplary embodiments with consideration of the figures. The figures show in:

FIG. 1	in a) and b) perspective cross-sectional views of assembled insulating glass units with a spacer profile, primary sealant and secondary sealant arranged therebetween according to a first and second embodiment,
FIG. 2	shows a side view, partially cut away, of a spacer frame bent from a spacer in the ideal condition,
FIG. 3	in a) and b) cross-sectional views of the spacer profiles according to the first and the second embodiment,
FIG. 4	an enlarged cross-sectional partial view of a spacer wall,
FIG. 5	in a) and b) diagrams showing the elemental concentrations of a stainless steel A (1.4310) according to a first sample,
Fig. 6	in a) and b) diagrams showing the elemental concentrations of a stainless steel B (1.4310) according to a second sample,
Fig. 7	in a) to c) diagrams showing a comparison between elemental concentrations of A and B,
Fig. 8	a table showing the elemental concentration of A,
Fig. 9	a table showing the elemental concentration of B,
Fig. 10	in a) and b) diagrams showing the elemental concentrations of a stainless steel C (1.4310) according to a third sample,
Fig. 11	in a) and b) diagrams showing the elemental concentrations of a stainless steel D (1.4301) according to a fourth sample,
Fig. 12	in a) and b) diagrams showing the elemental concentrations of a stainless steel E (1.4301) according to a fifth sample,
Fig. 13	in a) and b) diagrams showing the elemental concentrations of a stainless steel F (1.4310) according to a sixth sample,
Fig. 14	in a) to f) diagrams showing a comparison between elemental concentrations of C to F,
Fig. 15	a table showing the elemental concentration of C,
Fig. 16	a table showing the elemental concentration of D,
Fig. 17	a table showing the elemental concentration of E,
Fig. 18	a table showing the elemental concentration of F, and
Fig. 19	a diagram showing a comparison between the elemental concentrations of oxygen of A to F.

[0022] Embodiments of the present teachings will be described in greater detail below with references to the figures. The same features/elements are marked with the same reference numbers in all figures. For the purpose of clarity, all reference numbers have not been inserted into all figures.

[0023] The 3-dimensional (X, Y, Z) reference system shown in Fig. 1 is applicable to all figures and the description and the claims. The longitudinal direction corresponds to the direction Z, the traverse direction corresponds to the direction X and the height direction corresponds to the direction Y.

[0024] In Figs. 1 and 3, a so-called W-configuration of the spacer is shown in each a) view and a so-called U-configuration is shown in each b) view. A spacer according to a first embodiment will now be described with reference to Figs. 3a) and 3b).

[0025] In Figs. 3a) and 3b), the spacer is shown in cross-section perpendicular to a longitudinal direction, i.e. along a slice in the X-Y plane, and extends with this constant cross-section in the longitudinal direction. The spacer profile comprises a height h1 in the height direction Y and a width b1 in the direction X. The spacer profile 1 is comprised of a hollow profile body 10, which is formed from a first material. The first material is preferably an elastic-plastic deformable, poor heat conducting (insulating) material.

[0026] Herein, the term "elastic-plastic deformable" preferably means that elastic restoring forces are active in the material after a bending process, as is typically the case for synthetic materials for which only a part of the bending takes place with a plastic, irreversible deformation. Further, the term "poor heat conducting" preferably means that the heat conduction value [lambda] is less than or equal to about 0.3 W/(mK).

[0027] The first width b1 is preferably between 4mm and 40mm, more preferably, between 5mm and 30mm and further more preferably between 7.5 and 25mm, as for example, 14mm, 16mm or 20mm.

[0028] The first height h1 is preferably between 2mm and 20mm, more preferably, between 3mm and 15 and further more preferably between 4 and 10mm, as for example, 5mm, 6mm or 7mm.

[0029] The first material is preferably a synthetic material, more preferably a polyolefin and still more preferably polypropylene, polyethylene terephthalate, polyamide or polycarbonate. An example of such a polypropylene is Novolen(R) 1040K. The first material preferably has an E-modulus of less than or equal to about 2200 N/mm2 and a heat conduction value [lambda] less than or equal to about 0.3 W/(mK), preferably less than or equal to about 0.2 W/(mK). The walls (side wall, inner wall, outer wall) of the hollow profile body 10 may have the same first thickness d1. The first thickness d1 is preferably between 0.1mm and 5mm, more preferably between 0.2mm and 4mm, and further more preferably between 0.5mm and 1.2mm, for example, 0.7mm, 1mm or 1.1mm.

[0030] The profile body 10 is firmly bonded (e.g., fusion and/or adhesive bonded) with a one-piece metallic layer 30 forming a diffusion barrier. The metallic layer 30 is formed from a metal material. The second material is preferably a plastic deformable material. Herein, the term "plastic deformable" preferably means that practically no elastic restoring forces are active after the deformation. This is typically the case, for example, when metals are bent beyond their elastic limit (apparent yield limit).

[0031] Herein, the term "firmly bonded" preferably means that the profile body 10 and the metallic layer 30 are durably connected with each other, e.g. by co-extrusion of the profile body with the diffusion barrier film, and/or if necessary, by the application of an adhesive material. Preferably, the cohesiveness of the connection is sufficiently large that the materials are not separable in the peel test according to DIN 53282.

[0032] The profile body 10 comprises an inner wall 13 and an outer wall 14 separated in the height direction Y and two side walls 11, 12 that are separated by in the traverse direction X, and extend essentially in the height direction Y. The side walls 11, 12 are connected via the inner wall 13 and outer wall 14, so that a chamber 20 is formed for accommodating desiccant. The chamber 20 is defined on its respective sides in cross-section by the walls 11 to 14 of the profile body. The chamber 20 has a height h2 in the height direction Y and a width b2 in the traverse direction X.

[0033] The side walls 11, 12 are formed as attachment bases for attachment to the inner sides of the window panes 50, 52 (see Fig. 1). In other words, the spacer 10 is preferably adhered to the respective inner sides of the glass panes 50, 52 via these attachment bases (see Fig. 1) by using an adhesive material (primary sealant) 61, e.g., a butyl sealing compound based upon polyisobutylene. The interspace 54 between the window panes is thus defined by the two window panes 50, 52 and the spacer 10. On the side of the spacer 10 facing away from the interspace 54 between the window panes (in Fig. 1 in the height direction Y), a mechanically stabilizing sealing material (secondary sealant) is introduced into the remaining, empty space/groove between the inner sides of the window panes in order to fill the empty space/groove. The secondary sealant is, for example, based upon polysulfide, polyurethane or silicon. This sealant also protects the diffusion barrier layer from mechanical and/or other corrosive/degrading influences.

[0034] The inner wall 13 is defined herein as the "inner" wall, because it faces inward toward the interspace 54 between the glass panes 50, 52 in the assembled state of the insulating glass unit 1 as shown in Fig. 1. The outer wall 14, which is arranged in the height direction Y on the opposite side of the chamber 20, faces away from the interspace 54 between the glass panes 50, 52 in the assembled state and therefore is defined herein as the "outer" wall 14.

[0035] According to the W-configuration shown in Fig. 3a), the side walls 11, 12 each comprise a concave portion, when observed from outside of the chamber 20, which concave portion forms the transition of the outer wall 14 to the corresponding side wall 11, 12. As a result of this design, the heat conduction path via the metallic layer is elongated as compared to the U-configuration shown in Fig. 3b), even though the W- and U-configurations have the same height h1 and width b1. In exchange, the volume of the chamber 20, with the same width b1 and height h1, is slightly reduced.

[0036] Openings 15 are formed in the inner wall 13, independent of the choice of the material for the profile body, so that the inner wall 11 is not formed to be diffusion-proof. In addition or in the alternative, to achieve a non-diffusion-proof design, it is also possible to select the material for the entire profile body and/or the inner wall, such that the material permits an equivalent diffusion without the formation of the openings 15. However, the formation of the openings 15 is preferable. In any case, moisture exchange between the interspace between the glass panes and the desiccant in the chamber 20 in the assembled state is preferably ensured (see also Fig. 1). The diffusion barrier is constituted by the metallic layer 30 formed on the outer sides of the outer wall 14 and of the side walls 11, 12, which face away from the chamber 20. The layer 30 extends along the side walls in the height direction Y up to height h2 of the chamber 20. The metallic layer 30 comprises profiled elongation portions 31, 32, each having a profile 31 a, 32a.

[0037] Herein, the term "profile" preferably means that the elongation portion may not exclusively a linear elongation of the diffusion barrier film 30, but instead that a two-dimensional profile may be formed in the two-dimensional view of the cross-section in the X-Y plane, which profile is formed, for example, by one or more bends and/or angles in the elongation portion 31, 32. It is noted that the profiled elongation portions are optional.

[0038] On the other hand, for purely ornamental reasons, the metallic layer preferably should not be visible through the window panes of the assembled IGU. Therefore, the metallic layer preferably should be covered at the inner side by the material of the profile body.

[0039] In summary, the elongation portion may preferably be close to the inner side. Therefore, the region of the profile body (accommodation region), in which the elongation portion is located (is accommodated), preferably may be clearly above the mid-line of the profile in the height direction. In such case, the dimension (length) of the accommodation region from the inner side of the spacer profile in the Y-direction should not extend over more than 40% of the height of the spacer profile. In other words, the accommodation region 16, 17 comprises a height h3 in the height direction and the height h3 should be less than or equal to about 0.4 h1, preferably less than or equal to about 0.3 h1, more preferably less than or equal to about 0.2 h1 and still more preferably less than or equal to about 0.1 h1. Moreover, it is advantageous if the mass (weight) of the elongation portion comprises at least about 10% of the mass (weight) of the remaining part of the diffusion barrier film, which is above the mid-line of the spacer profile in the height direction, preferably at least about 20%, more preferably at least about 50% and still more preferably about 100%.

[0040] Furthermore, the metallic layer 30 additionally also preferably acts as a reinforcement element. The preferred first metallic material for the diffusion barrier layer 30 is stainless steel having a thermal conductivity value of $\lambda \leq$ about 50 W/(m K), preferably $\leq$ about 25 W/(m K), and more preferably $\leq$ about 15 W/(m K) and more than 5 W/(m K)

[0041] The metallic layer 30 has a second thickness d2, which is between 0.5 mm and 0.001 mm, preferably between 0.20 mm and 0.01 mm, more preferably between 0.10 mm and 0.01 mm, and still more preferably between 0.09 mm and 0.04 mm, for example, 0.05 mm, 0.08 mm, or 0.09 mm.

[0042] The maximum thickness can be selected in accordance with the desired thermal conductivity value. The thinner the film is, the better the "warm edge"-conditions are fulfilled. In the embodiments shown in Fig. 3a) and b), thicknesses in the range of 0.10 mm to 0.01 mm are preferred.

[0043] An example for the metallic layer is a stainless steel film 1.4016, 1.4301, 1.4310, or 1.4372 according to DIN EN 1008812 having a thickness of 0.1 mm or 0.09 mm.

[0044] As far as the term "diffusion resistance", or rather "diffusion resistant" (or (diffusion) impermeability, diffusion proof etc.) are utilized with respect to the spacer profile or materials forming the spacer profile, vapour diffusion impermeability as well as also gas diffusion impermeability for the gases relevant herein (for example nitrogen, oxygen, water, etc.) are meant to be encompassed within the meaning thereof. The utilized materials are considered to be gas or vapour diffusion resistant or rather impermeable, if not more than 1% of the gases in the interspace 54 between the panes can leak out within the period of one year. Furthermore, diffusion resistant is also equated to a low permeability in the sense of that the corresponding test norm EN1279 part 2 + 3 is fulfilled. That means, the finished spacer profile or insulating glass unit (or insulating window unit) having such a spacer profile should fulfil the test norm EN1279 part 2 + 3.

[0045] According to the first embodiment, the metallic layer is made of a normal, commercially available stainless steel which is exposed to an oxidation treatment process. As stated above, such a metallic layer will be referred to as oxide stainless steel in the following. In comparison thereto, stainless steel, which is not exposed to an oxidation treatment process, will be referred to as normal stainless steel.

[0046] Fig. 4 shows an enlarged cross-sectional partial and simplified view of a wall (here the outer wall 14) of the hollow profile 10 comprising the metallic layer 30. As it can be further seen from Fig. 4 in a simplified manner, the metallic layer 30 itself has different zones/layers 30a, 30b due to the following: in the oxidation treatment process, an oxide layer 30a is oxidized/created onto or on an outer surface (facing away from the chamber 20) of a basic layer 30b of the stainless steel material up to certain third thickness d3 from the outer surface of the basic layer 30b. Accordingly, the chemical compositions of the oxide layer 30a and the basic layer 30b differ from each other although the same together are referred to as the metallic layer 30.

[0047] The chemical composition within the oxide layer 30a changes with the distance from the external surface 30c. The external surface 30c is the surface of the metallic layer 30, which faces away from the chamber 20. The greatest changes take place near and/or on the surface 30c. With an increase of the distance from the surface 30c, the changes reduce more and more. In a certain third distance (depth) d3 from the surface 30c, basically only the basic steel composition is present. As it will be described later, some elemental concentrations change with an asymptotic curve from the surface 30c or from anywhere within the oxide layer 30a to the beginning of the basic layer 30b.

[0048] For simplification, the third distance d3, and therefore, the border between the zone called oxide layer 30a and the zone called basic layer 30b is determined in the following as follows: at the third distance d3 from the surface 30c, the elemental concentration of O (Oxygen) is equal to 2at%. This means, the transition between oxide layer 30a and the basic stainless steel layer 30b is determined by the elemental content of oxygen measured with the below described method. In other words, the oxide layer 30a is considered to be present in case an elemental concentration of oxygen is equal to or above 2at% and the basic layer 30b is considered to be present in case an elemental concentration of oxygen is below 2at%. In general, the stainless steel material has basically 0at% elemental concentration of oxygen. However, due to the below described measurement method, an elemental concentration below 2at% is considered to be present in the basic layer.

[0049] Thus, the oxide layer has the third thickness d3, which is, depending on the oxidation treatment process, preferably between 10nm and 400nm, more preferably between 30nm and 100nm, and further more preferably between 70nm and 85nm, as, for example, 80nm, 84nm, or 86nm.

[0050] The remaining basic layer has a fourth thickness d4, which can be derived by the following formula:

$d4 = d2 - d3$

[0051] The oxidation treatment process is, according to the present embodiment, performed in the last annealing step of stainless steel manufacturing process by bringing the stainless steel sheets into contact with a specific atmosphere. For example, the atmosphere is comprised of Nitrogen and/or Hydrogen. Alternatively, the oxidation treatment process may be performed by a chemical treatment.

[0052] In case of oxidation by exposing to a specific atmosphere, the surface characteristics of the oxidized layer are due to the composition of said gas atmosphere. In particular, the atmosphere is made less reducing, and therefore more oxidizing, by increasing the amount of Nitrogen. In this way, formation of hydroxyl groups / metal oxides is made possible.

[0053] Figs. 5, 6 and 10 to 13 show diagrams of elemental concentrations [at%] at different distances from the surface of different stainless steel materials A to F as samples. Fig. 8, 9 and 15 to 18 show corresponding tables including the measurement values.

[0054] Figs. 6, 10, 12 and 13 refer to the samples B, C, E and F for stainless steel materials which were exposed to a special oxidation treatment process. Figs. 5 and 11 refer to the samples A and D for stainless steel materials which were not exposed to a special oxidation treatment process. However, the manufacturing process of sample A leads also to the greater thickness of an oxide layer than it is the case for normal stainless steels such that sample A can also be considered as oxide stainless steel. Sample D is a sample for a normal stainless steel being not exposed to any oxidation treatment.

[0055] Figs. 7, 14 and 19 show diagrams wherein the elemental concentrations of the different samples A to F can be compared.

[0056] The investigations (determination of elemental concentrations) have been performed with a PHI 5500 ESCA spectrometer using monochromatic AlKα-radiation. The spot size amounted to approx. 0.8 mm. ESCA (Electron Spectroscopy for Chemical Analysis) provides semiquantitative information (at%) about the surface elemental composition and chemical binding in the topmost nm of a sample surface.

[0057] For the sputtering experiments a focused 3 keV Ar ion beam scans a surface area of approx. 4.0 x 5.5 mm. During this process material was sputtered off and the surface composition was determined alternately. The sputtering ratio for the estimation of the sputter depth has been determined to approx. 2.98 nm/min (corresponding to a reference sample of tantalum pentoxide on tantalum).

[0058] Results are shown in terms of sputter-time (see "minute" on the x-axis). It is possible to convert the graphs in depth profiles by multiplying the values on the x-axis by the above mentioned sputtering ratio of 2.98 nm/min. This means, 1 min on the horizontal axis of the diagrams corresponds to a distance 2.98nm from the outer surface 30c, wherein the surface 30c is present at 0 min (=surface corresponds to the vertical axis).

[0059] It has been found that the adhesion properties are improved if preferably

an elemental concentration of oxygen is continuously above or equal to 30at% in a region between the outer surface 30c of the metallic layer 30 and 3nm distance to the outer surface 30c of the metallic layer 30a, and/or

an elemental concentration of oxygen is continuously above or equal to 20at% in a region between the outer surface 30c of the metallic layer 30 and 6nm distance to the outer surface 30c of the metallic layer 30a, and/or an elemental concentration of oxygen is continuously above or equal to 10at% in a region between the outer surface 30c of the metallic layer 30 and 15nm distance to the outer surface 30c of the metallic layer 30a, and/or the oxide layer 30a extends at least between the surface 30c of the metallic layer 30 and preferably 15nm distance, more preferably 25nm distance, and further more preferably 30nm distance from the surface 30c of the metallic layer 30 if the oxide layer 30a is considered to be present in case an elemental concentration of oxygen is equal to or above 2at% and the basic layer 30b is considered to be present in case an elemental concentration of oxygen is below 2at%.

[0060] Specifically the elemental concentrations of the below described samples A, B, C, E and F have been found to significantly increase the bonding characteristics/properties versus the sample D.

[0061] The metallic material of sample A is a 1.4310 oxide stainless steel with a thickness d2 of 0.09 mm. Sample A has a specific manufacturing process increasing the oxide layer. The metallic material of sample B is a 1.4310 oxide stainless steel with a thickness d2 of 0.09 mm.

[0062] The metallic material of sample C is a 1.4310 oxide stainless steel with a thickness of 0.09 mm. The metallic material of sample D is a 1.4301 standard stainless steel with a thickness of 0.1 mm. The metallic material of sample E is a 1.4310 oxide stainless steel with a thickness of 0.09 mm. The metallic material of sample F is a 1.4301 oxide stainless steel with a thickness of 0.09 mm.

[0063] With the above definition of the thickness d3 of the oxide layer 30a, it can be seen, in particular from the comparison diagram in Fig. 19 (but also from the diagrams in Figs. 7a , and 14b and the corresponding measurement tables) that an almost constant elemental concentration of Oxygen (O) and Iron (Fe) is observable for sample A after a sputtering time of 10.5 minutes, for sample B after a sputtering time of 33 minutes, for sample C after a sputtering time of 37 minutes, for sample D after a sputtering time of 3.5 minutes, for sample E after a sputtering time of 60 minutes and for sample F after a sputtering time of 9.5 minutes.

[0064] This means, in terms of depth profiles, that in sample A below a first thickness of 31 nm (10.5 min x 2.98 nm/min) the basic steel composition is detected or, in other words, the superficial layer where hydroxyl groups / metal oxides are present is as thick as 31 nm.

[0065] On the other hand, for the oxide stainless steel according to sample B, the basic steel composition is detected at a depth of 98 nm (33 min x 2.98 nm/min) or, in other words, the oxide layer where hydroxyl groups / metal oxides are present, is as thick as 98 nm.

[0066] Furthermore, for the oxide stainless steel according to sample C, the basic steel composition is detected at a depth of 110 nm (37 min x 2.98 nm/min) while for the oxide stainless steel according to sample E, the basic steel composition is detected at a depth of 178.8 nm (60 min x 2.98 nm/min). In contrast, for the normal stainless steel according to sample D, the basic steel composition is detected at a depth of 10 nm (3.5 min x 2.98 nm/min). Furthermore, for the oxide stainless steel according to sample F, the basic steel composition is detected at a depth of 28 nm (9.5 min x 2.98 nm/min).

[0067] Accordingly, a significant difference (28nm vs. 10nm) in the third thickness d3 of the oxide layer is present between normal stainless steels and oxide stainless steels. Such an increased thickness of the oxide layer leads to improved adhesion properties, as stated above.

[0068] As it can be seen from Figs. 19, 7a and 14b that the above conditions which must be fulfilled for the improved adhesion properties are fulfilled in case of sample A, B, C, E and F but not fulfilled in case of same D. Sample D does not have an elemental concentration of oxygen being continuously higher than 20at% in the region between the surface of the oxide layer 30a and a depth of 6nm.

[0069] Furthermore, it can be seen, in particular, from Figs. 19, 7a and 14a, that the oxide stainless steels according to samples A, B, C, E and F which have the improved adhesion properties, have within a sputter time region of

preferably 2 min to 20 min an average decrease rate of the elemental concentration of oxygen between 0.83at%/min and 2.47at%/min,

preferably 4 min to 6 min a basically linear decrease rate of the elemental concentration of oxygen with an average decrease rate higher than or equal to 0.9at%/min, preferably between 0.9at%/min and 2.8at%/min.

[0070] Furthermore, preferably the oxide layer 30a includes a concentration of at least one metal oxide and/or of hydroxyl groups which is at least 10% higher than in the basic layer 30b, and/or which increases the surface tension by at least 20% in comparison to the basic layer 30b.

[0071] Furthermore, sample B, C and E, as samples with a further improved characteristic, show an elemental concentration of oxygen greater than 20at% in a time region between 0 and 13min, whereas the same is above 10at% in a time region between 0 and 18min.

[0072] Comparing now both Cr profiles of sample A and B, is it possible to see a higher concentration for sample B. After 11 minutes of sputtering, a quite constant concentration of Cr can be found for sample A. For example sample B an analogous Cr concentration level is achieved after a sputtering time of 18 minutes.

[0073] Further remarkable difference between the two steel samples A and B can be noticed regarding Mn because sample B shows higher concentrations of this element in the oxide layer.

[0074] This general trend is not observable for Ni and Si. In comparison with sample A, a smaller Ni concentration level is observable for sample B within the first 12 minutes of sputtering. Sample A shows higher Si concentrations in the depth profile than sample B. These Si concentrations may be a result of residues of metal working fluids, for example.

[0075] Basically the same analysis of the elemental concentrations can be done for the other samples and elements.

[0076] Furthermore, it is noted that the hollow spacer profile can have basically any shape and is not restricted to the shapes shown in Figs. 1 and 3. Furthermore, the material for the hollow profile body may also be a metallic material, onto which the metallic layer is applied. Furthermore, the hollow profile body and the metallic layer may be integrally formed of a metallic material whereas the oxide layer is formed on its surface. This means, the spacer may be formed only of stainless steel and is optionally integrally formed. Furthermore, the spacer may be formed of a U-shaped profile (=no hollow profile body) of synthetic or metal material comprising a metallic layer closing the U to an O (i.e. connecting the upper ends of the legs of the U). In this case the metallic layer and/or the metal material of the profile may be oxidized.

[0077] It is explicitly stated that all features disclosed in the description and/or the claims are intended to be disclosed separately and independently from each other for the purpose of original disclosure as well as for the purpose of restricting the claimed invention independent of the composition of the features in the embodiments and/or the claims. It is explicitly stated that all value ranges or indications of groups of entities disclose every possible intermediate value or intermediate entity for the purpose of original disclosure as well as for the purpose of restricting the claimed invention, in particular as limits of value ranges.

Claims

1. A spacer for an insulating glass unit (1) with at least two glass panes (50, 52), comprising
a metallic layer (30),
wherein
the metallic layer (30) has a basic layer (30b) and at least one oxide layer (30a), and the basic layer (30b) is made of stainless steel, and
the oxide layer (30a) is provided on the basic layer by oxidation,
the oxide layer (30a) provides improved adhesion properties in comparison to the basic layer (30b).

2. The spacer according to claim 1, wherein
an elemental concentration of oxygen is continuously above or equal to 20at% in a region between the outer surface 30(c) of the metallic layer (30) and 6nm distance to the outer surface (30c) of the metallic layer (30).

3. The spacer according to claim 1 or 2, wherein
an elemental concentration of oxygen is continuously above or equal to 10at% in a region between the outer surface 30(c) of the metallic layer (30) and 15nm distance to the outer surface (30c) of the metallic layer (30).

4. The spacer according to any one of claims 1 to 3, wherein
the oxide layer (30a) extends at least between the surface (30c) of the metallic layer (30) and 25nm distance from the surface (30c) of the metallic layer (30) if the oxide layer (30a) is considered to be present in case an elemental concentration of oxygen is equal to or above 2at% and the basic layer (30b) is considered to be present in case an elemental concentration of oxygen is below 2at%,

5. The spacer according to any one of claims 1 to 4, further comprising
a hollow profile body (10) having an inner wall (13), an outer wall (14) and side walls (11, 12) defining a chamber (20), where the inner wall (13) is adapted to face an interspace (54) formed between the glass panes (50, 52) and the side walls (11, 12) are adapted to face the surface of the panes (50, 52) and the outer wall (14) is adapted to face away from the interspace (54) in an assembled stated of the insulating glass unit (1), and
the basic layer (30b) is provided on at least parts of the outer wall (14) and/or of the side walls (11, 12) on the outer side of the hollow profile body (10),
the oxide layer (30a) is provided on the outer side of the basic layer (30b) and forms, at least partly, the outer surface of the spacer,
the oxide layer (30a) is adapted to be in contact with a sealant (61, 62) in an assembled insulating glass unit (1).

6. The spacer according to any one of claims 1 to 5, wherein
the oxide layer (30a) comprises hydroxyl groups and metal oxides.

7. The spacer according to any one of claims 1 to 6, wherein
in comparison to the stainless steel material of the basic layer (30b), the oxide layer (30a) has a higher content of at least one metal oxide other than Fe oxide and/or a higher content of hydroxyl groups and/or a higher surface tension.

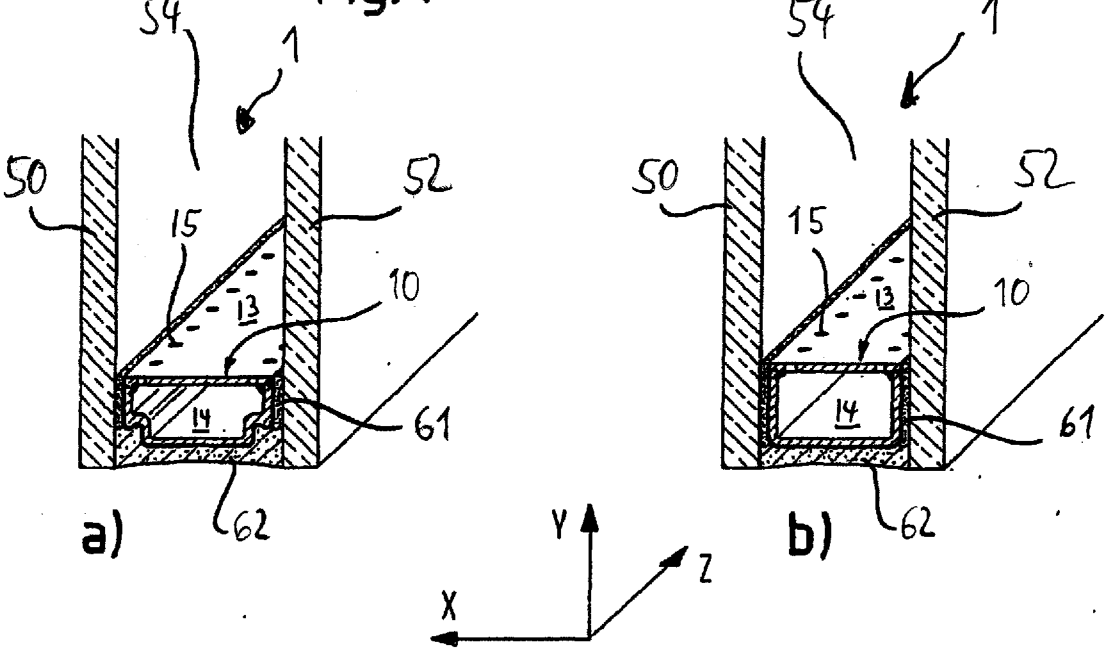
8. The spacer according to claim 7, wherein
the oxide layer (30a) includes a concentration of at least one metal oxide and/or of hydroxyl groups which is at least 10% higher than in the basic layer (30b), and/or which increases the surface tension by at least 20% in comparison to the basic layer (30b).

9. The spacer according to any one of claims 1 to 8, wherein the elemental concentration of oxygen between 12nm to 18 nm distance from the surface (30c) within the metallic layer (30) decreases basically linearly with an average decrease rate being higher or equal to 0.3at%/nm.

10. The spacer according to any one of claims 1 to 9, wherein
the metallic layer (30) has a thickness of at least 1 μm.

11. Insulating glass unit (1) comprising
a spacer (10) according to one any one of claims 1 to 10,
at least two glass panes (50, 52),
a sealant (61, 62),
wherein
the spacer (10) is arranged between the glass panes (50, 52) and connected thereto via the sealant (61, 62), respectively,
the sealant (61, 62) adheres to the oxide layer (30a) of the spacer (10).

Fig. 1



a)

b)

Fig. 2

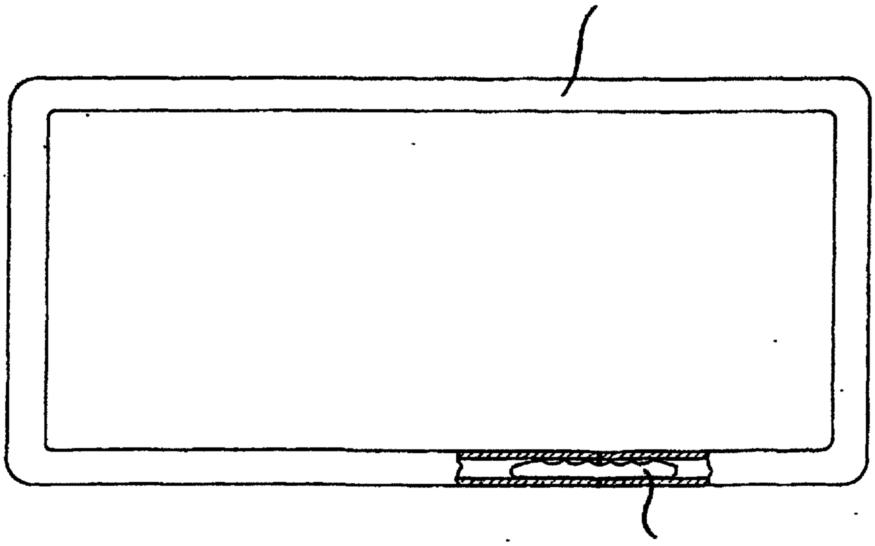
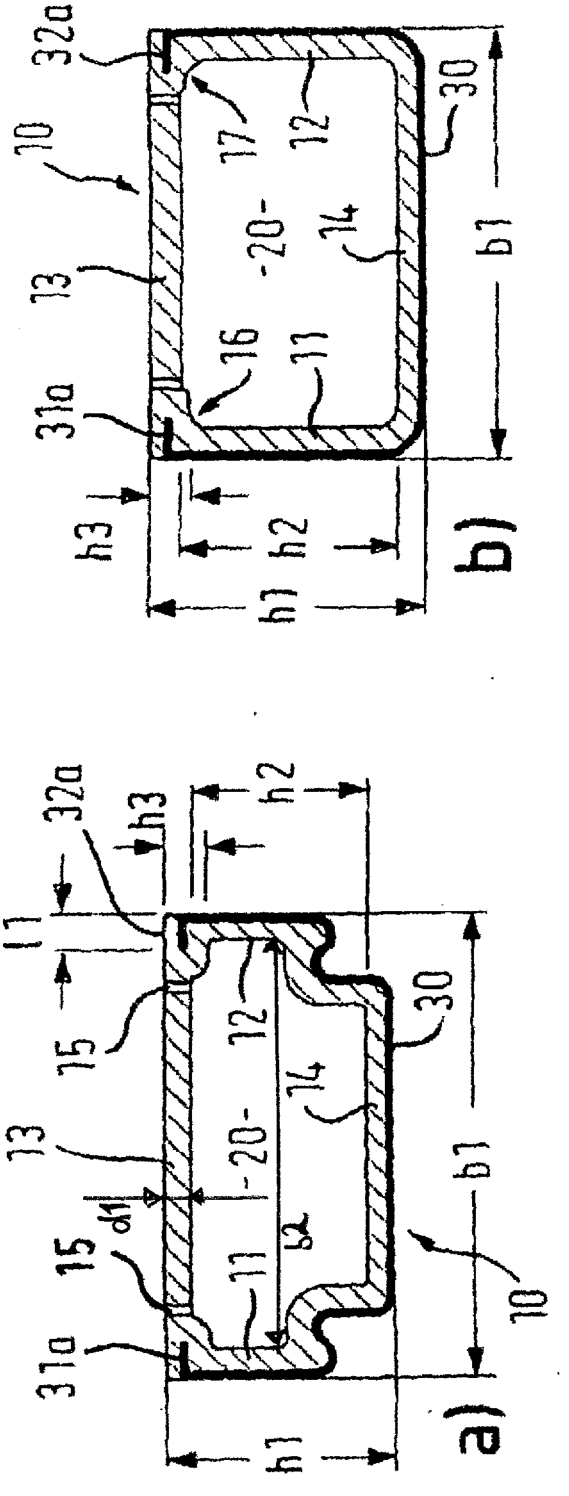


Fig. 3



a)

b)

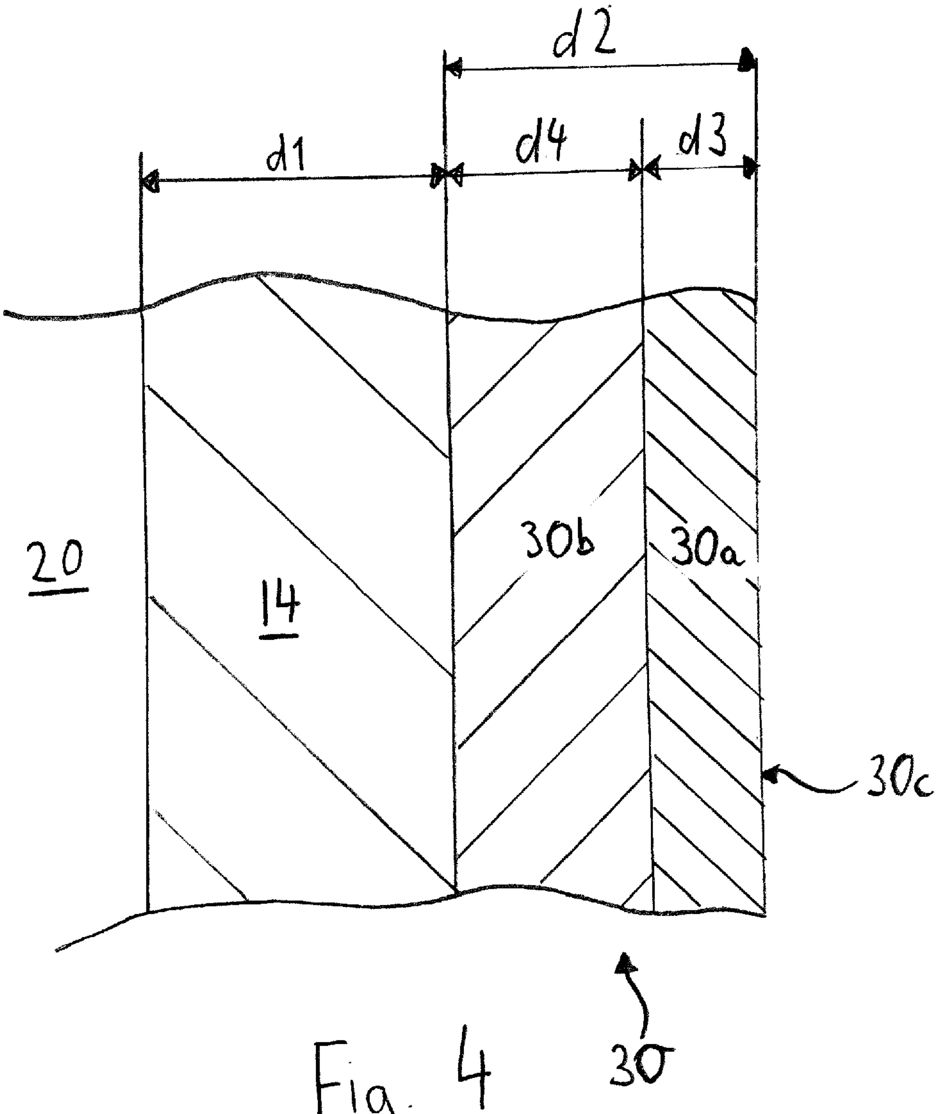


Fig. 4

Sample A **Typ 1.4310 standard**

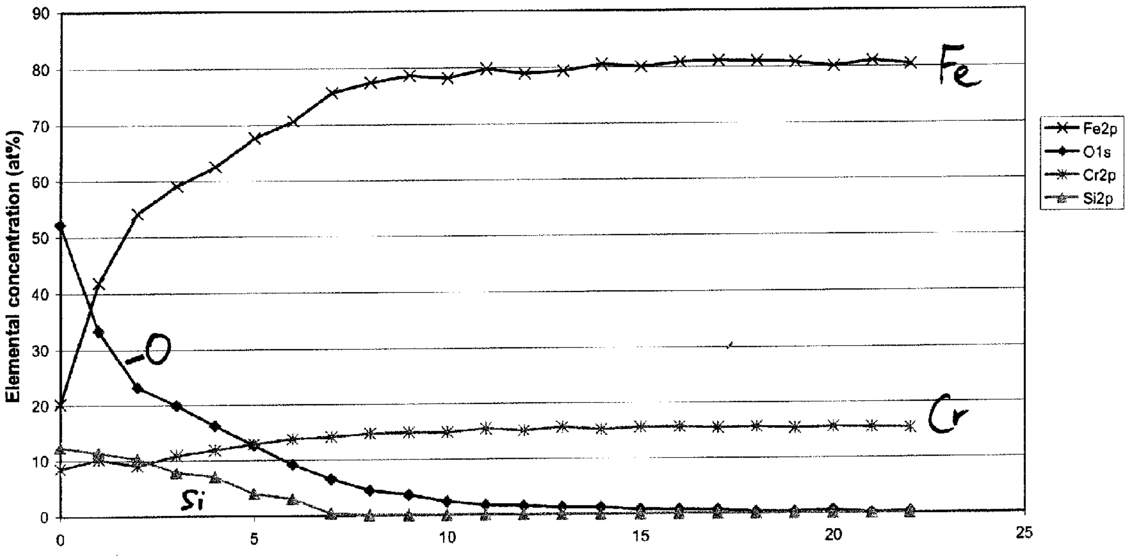


Fig. 5a

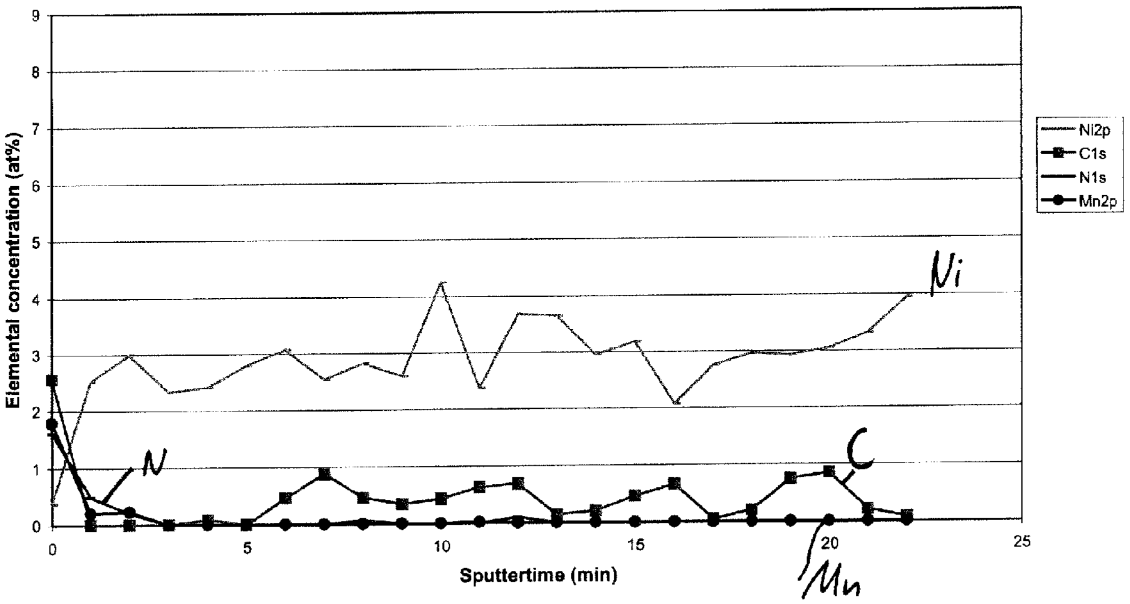


Fig. 5b

Sample B **Typ 1.4310**

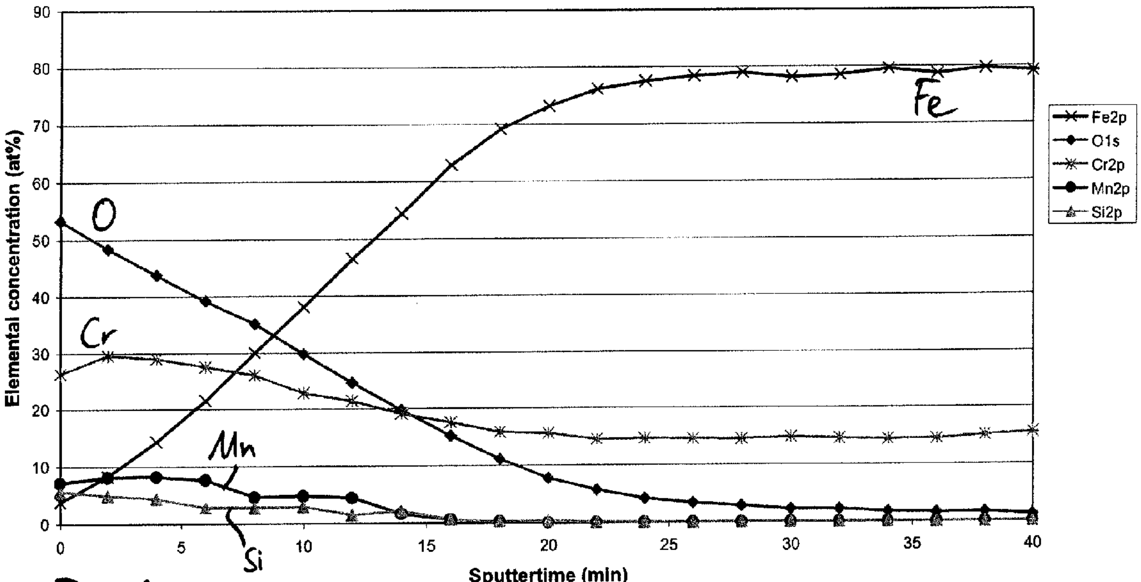


Fig. 6a

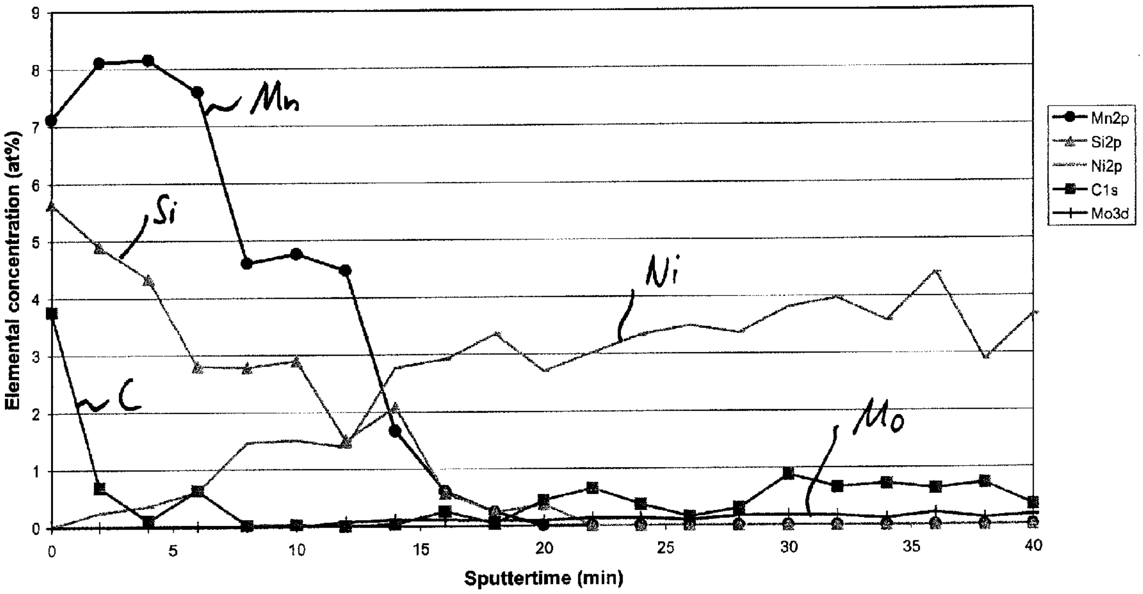


Fig. 6b

Comparison of Sample A and B

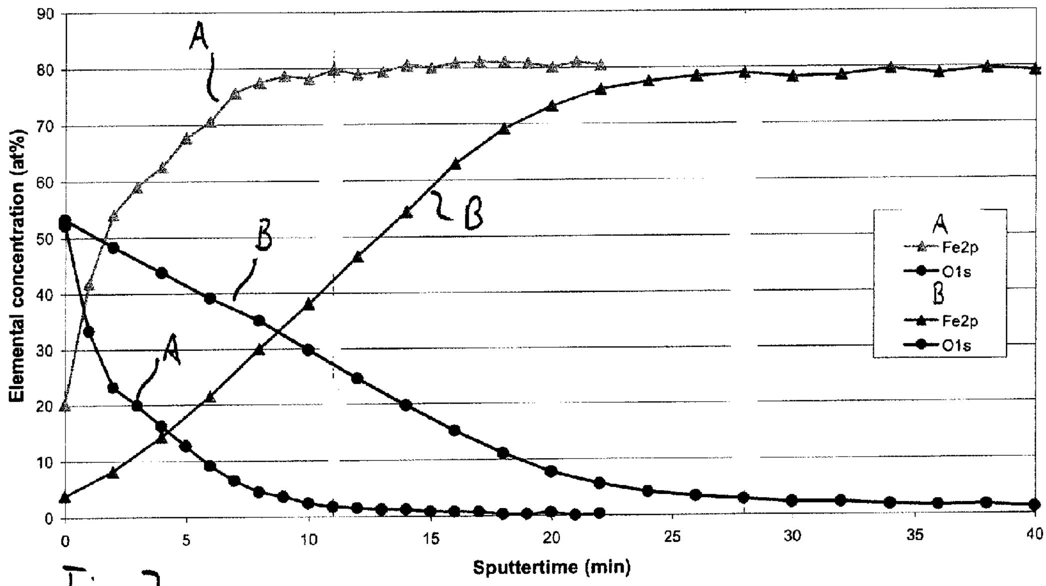


Fig. 7a

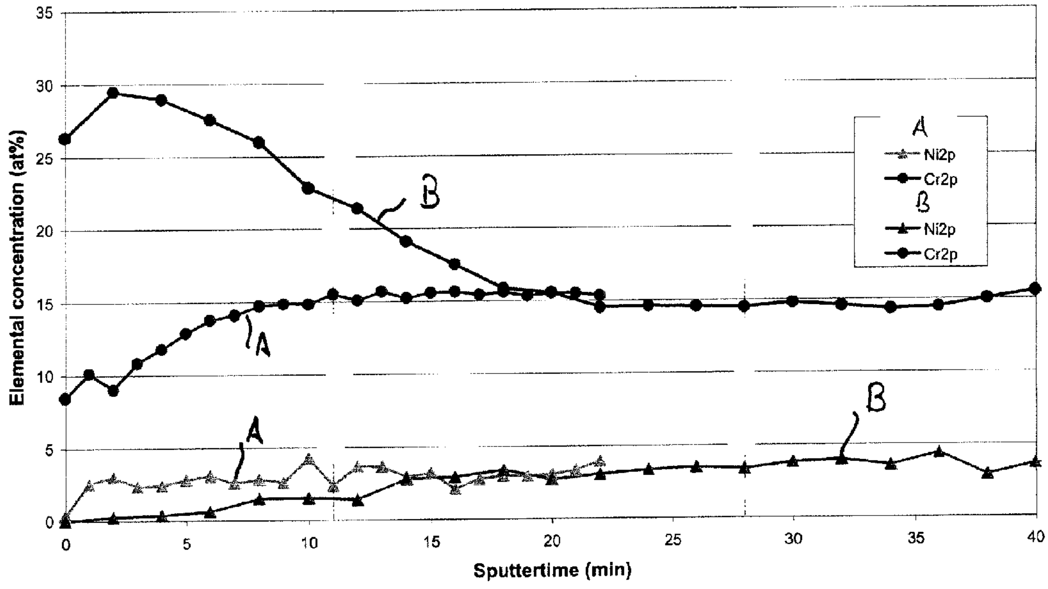


Fig. 7b

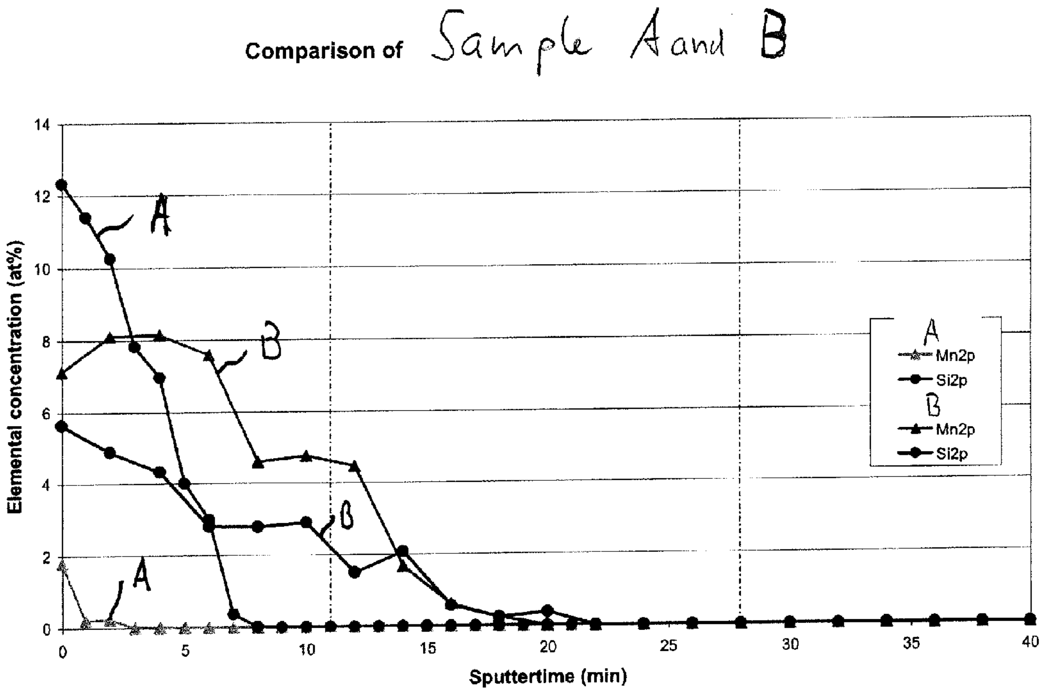

Comparison of Sample A and B
Elemental concentration (at%)
14
12
10
8
6
4
2
0
0
5
10
15
20
25
30
35
40
Sputtertime (min)
A
B
B
A
A
Mn2p
Si2p
B
Mn2p
Si2p

Fig. 7c

Typ 1.4310

Sample A		Sputtertime [min]	Elemental concentration (at%)								
			C	O	N	Si	Fe	Cr	Mn	Ni	Sn
		0	2.6	52.2	1.6	12.3	20.2	8.4	1.8	0.4	0.5
		1	-	33.3	0.5	11.4	41.9	10.1	0.2	2.5	0.1
		2	-	23.2	0.2	10.3	54.2	9.0	0.2	3.0	-
		3	-	19.9	-	7.8	59.1	10.8	-	2.3	-
		4	0.1	16.2	-	7.0	62.5	11.8	-	2.4	-
		5	-	12.7	-	4.0	67.7	12.9	-	2.8	-
		6	0.5	9.1	-	3.0	70.6	13.8	-	3.1	-
		7	0.9	6.5	-	0.4	75.6	14.1	-	2.5	-
		8	0.5	4.4	0.1	#	77.5	14.7	-	2.8	-
		9	0.3	3.6	-	-	78.6	14.9	-	2.6	-
		10	0.4	2.4	-	-	78.1	14.8	-	4.3	-
		11	0.6	1.7	-	-	79.8	15.5	-	2.4	-
		12	0.7	1.5	0.1	-	78.9	15.1	-	3.7	-
		13	0.1	1.2	-	-	79.3	15.7	-	3.7	-
		14	0.2	1.2	-	-	80.5	15.2	-	3.0	-
		15	0.5	0.8	-	-	80.0	15.6	-	3.2	-
		16	0.7	0.8	-	-	80.9	15.7	-	2.1	-
		17	#	0.7	-	-	81.1	15.4	-	2.8	-
		18	0.2	0.3	-	-	81.0	15.6	-	3.0	-
		19	0.8	0.3	-	-	80.8	15.3	-	2.9	-
		20	0.9	0.6	-	-	80.0	15.6	-	3.1	-
		21	0.2	-	-	-	81.0	15.5	-	3.3	-
		22	0.1	0.3	-	-	80.4	15.3	-	3.9	-

- no detection possible
in traces (< 0.05 at%) detectable

Fig. 8

ESCA

Typ 1.4310

Sample B		Sputtertime [min]	Elemental concentration (at%)							
			C	O	Si	Fe	Cr	Mn	Mo	Ni
		0	3.8	53.3	5.7	3.9	26.3	7.1	-	-
		2	0.7	48.4	4.9	8.2	29.5	8.1	-	0.2
		4	0.1	43.8	4.3	14.3	29.0	8.2	-	0.4
		6	0.6	39.2	2.8	21.5	27.6	7.6	-	0.6
		8	#	35.1	2.8	30.0	26.0	4.6	-	1.5
		10	#	29.8	2.9	38.1	22.8	4.8	-	1.5
		12	-	24.6	1.5	46.6	21.4	4.5	0.1	1.4
		14	#	19.8	2.1	54.5	19.1	1.7	0.1	2.8
		16	0.3	15.1	0.6	62.9	17.5	0.6	0.1	2.9
		18	#	11.1	0.2	69.1	15.8	0.2	0.1	3.4
		20	0.4	7.7	0.4	73.1	15.6	-	0.1	2.7
		22	0.7	5.6	-	76.1	14.5	-	0.1	3.0
		24	0.4	4.1	-	77.5	14.6	-	0.1	3.3
		26	0.2	3.3	-	78.4	14.6	-	0.1	3.5
		28	0.3	2.8	-	78.9	14.5	-	0.2	3.4
		30	0.9	2.2	-	78.1	14.8	-	0.2	3.8
		32	0.7	2.2	-	78.5	14.6	-	0.2	4.0
		34	0.7	1.7	-	79.5	14.3	-	0.1	3.6
		36	0.6	1.5	-	78.7	14.5	-	0.2	4.4
		38	0.7	1.6	-	79.6	15.0	-	0.1	2.9
		40	0.4	1.2	-	79.1	15.5	-	0.2	3.7

- no detection possible
in traces (< 0.05 at%) detectable

Fig. 9

Sample C

Typ 1.4310

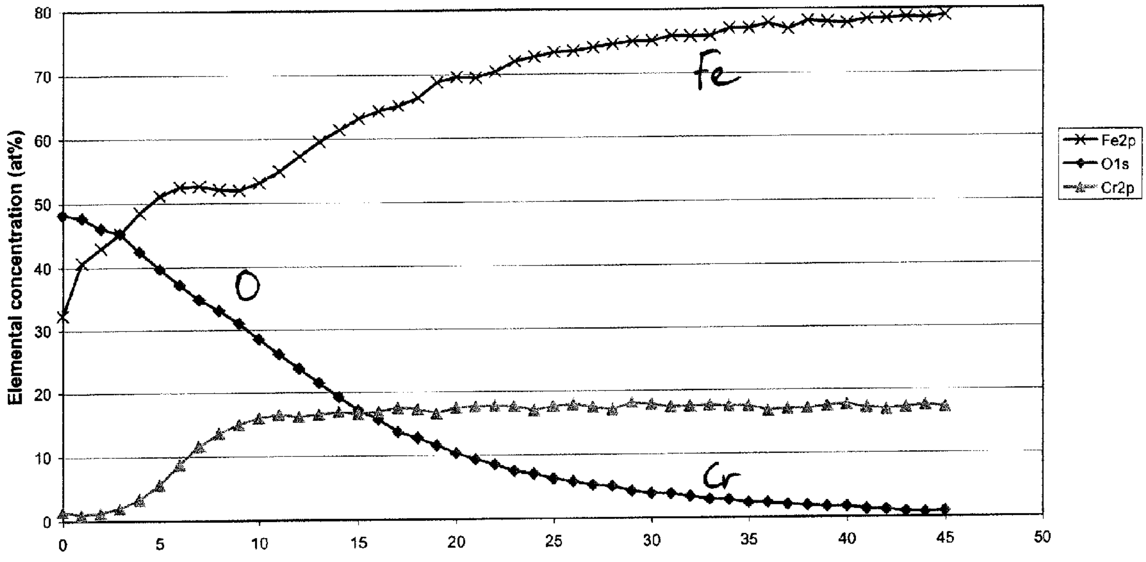


Fig. 10a

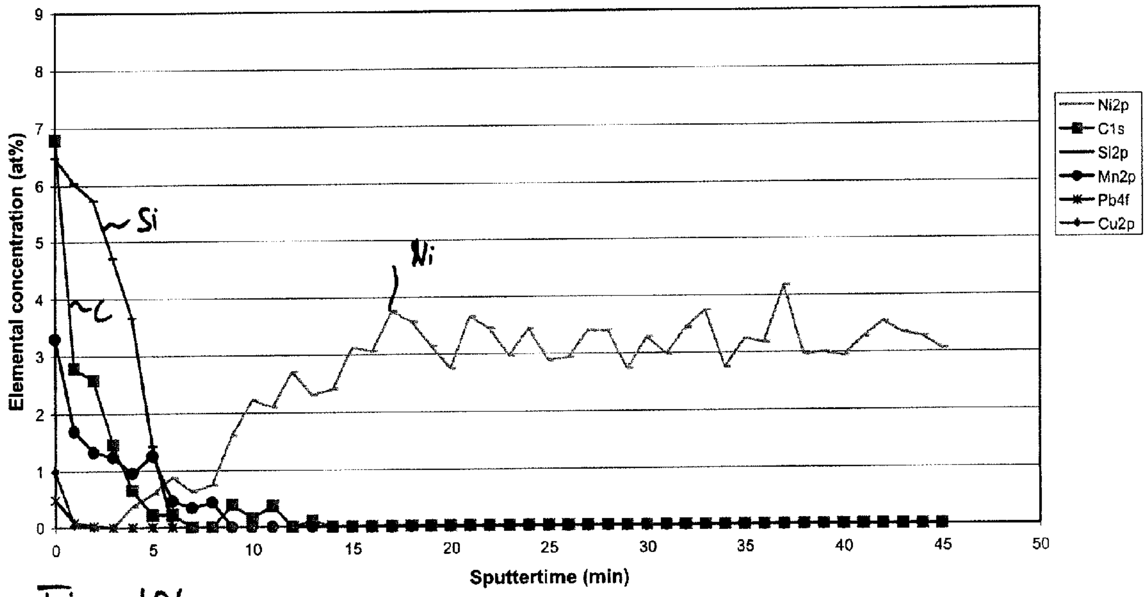


Fig. 10b

Sample D

Typ 1.4301

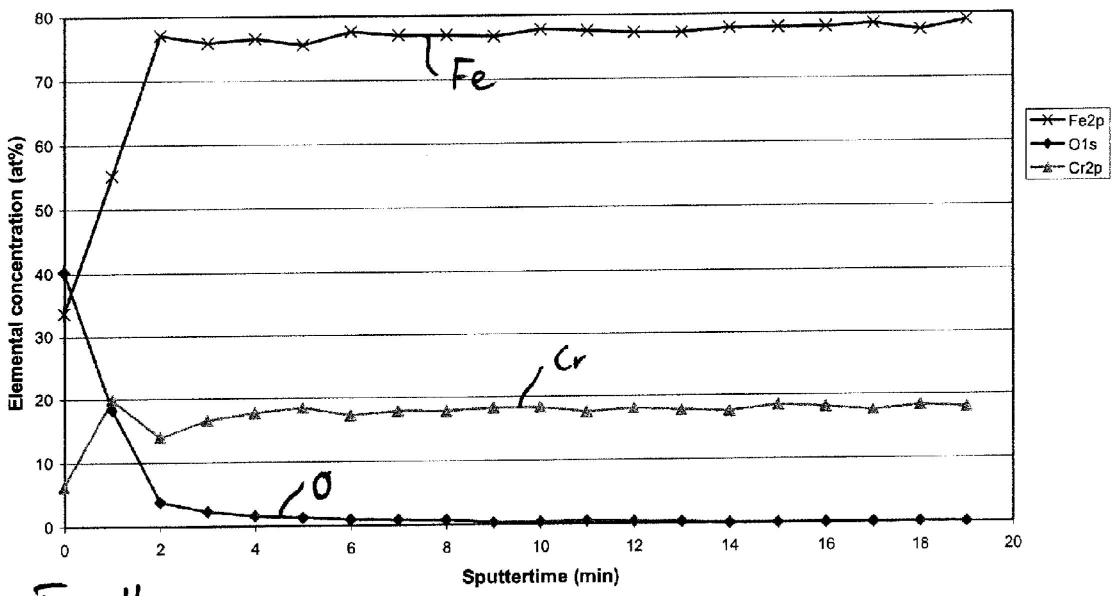


Fig. 11a

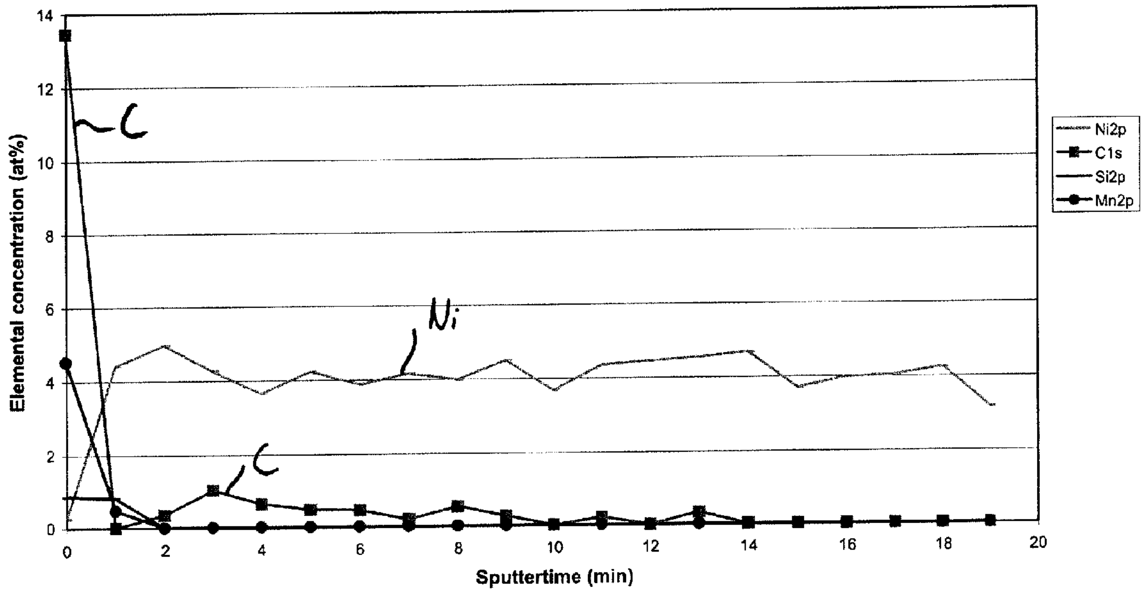


Fig. 11b

Sample E

Typ 1.4301

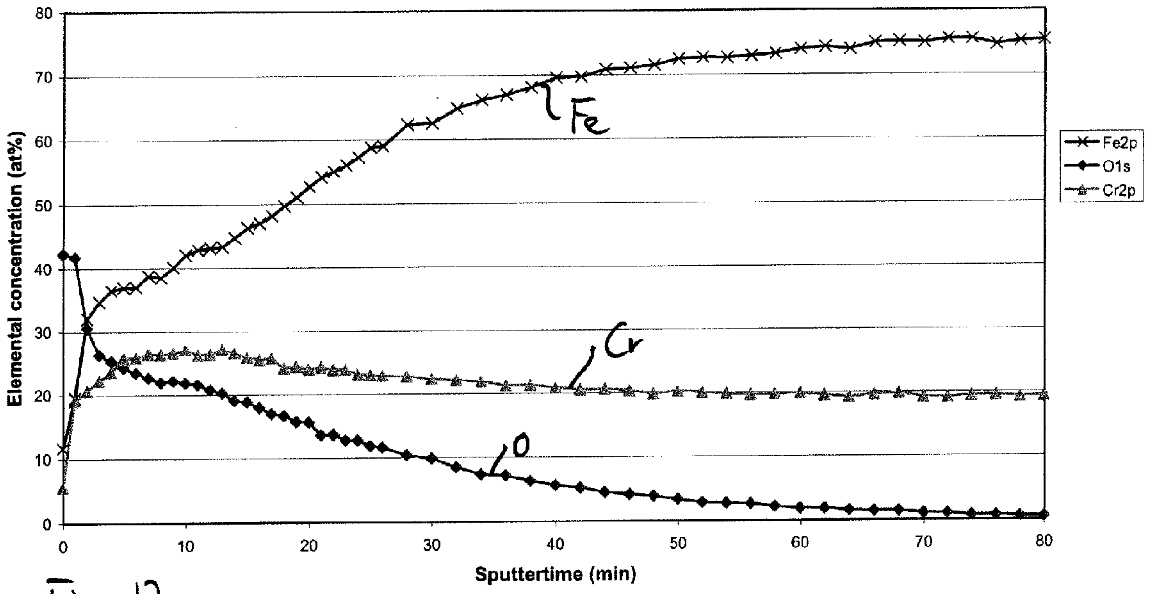


Fig. 12a

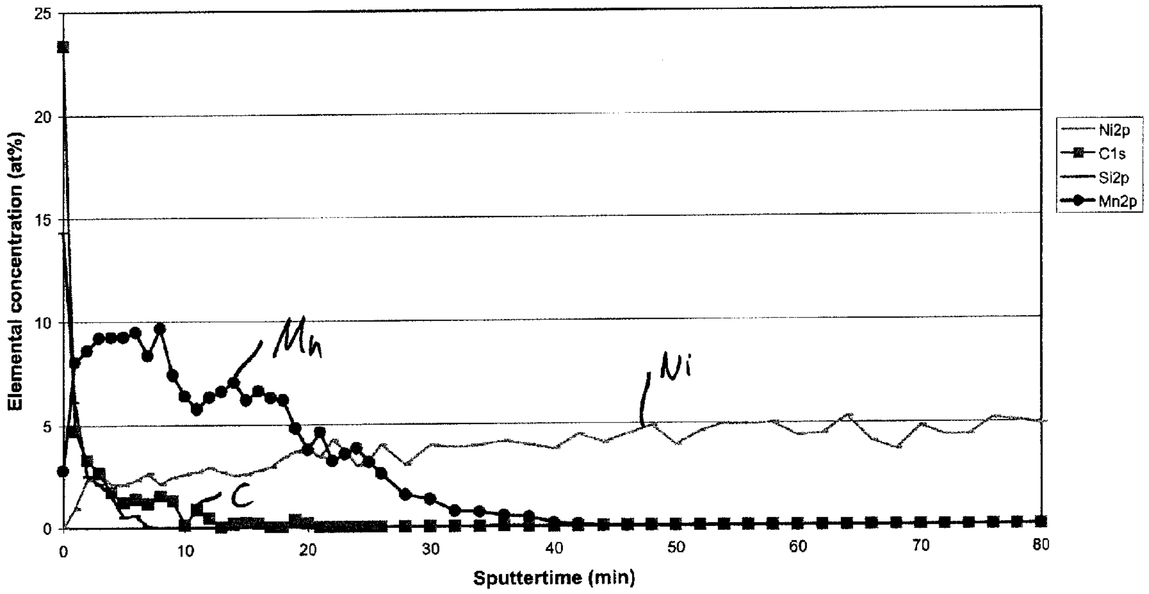


Fig. 12b

Sample F

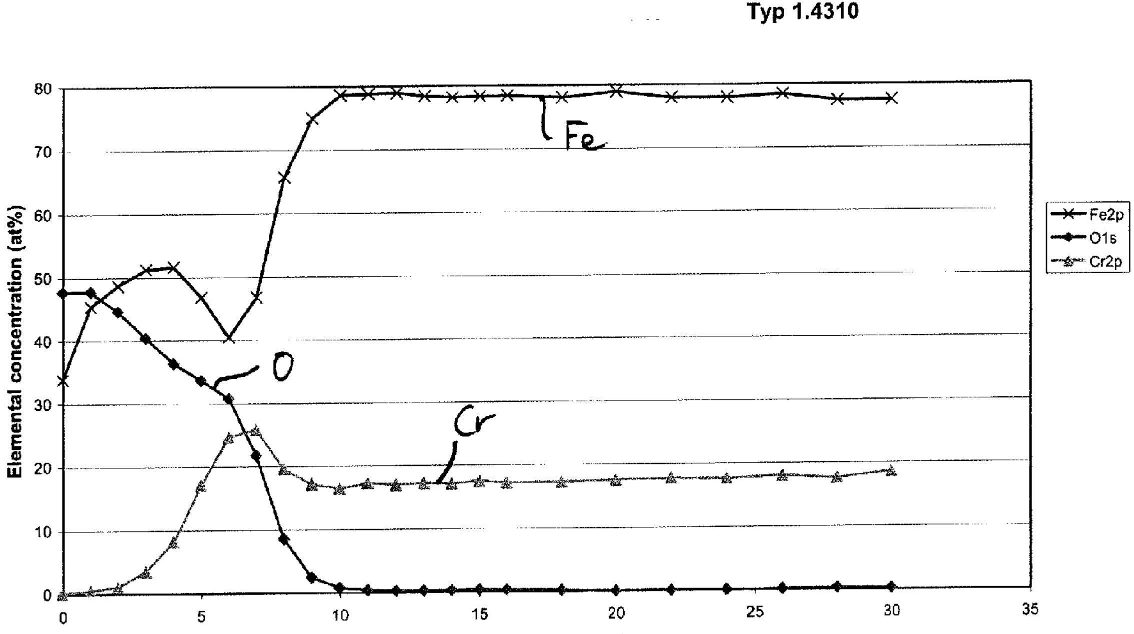


Fig. 13a

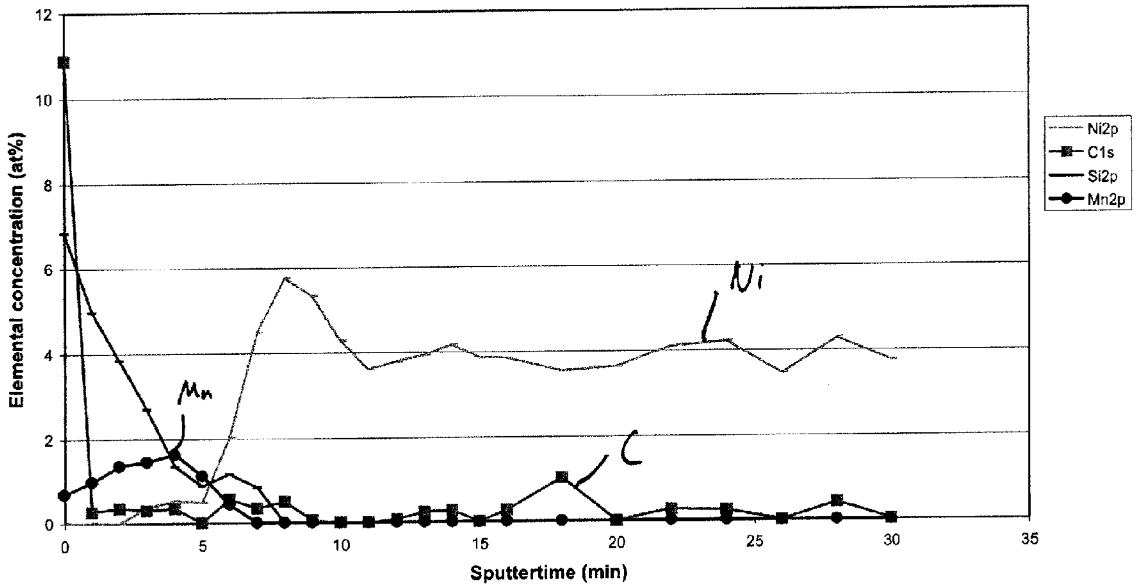


Fig. 13b

Comparison of Fe in Samples C to E

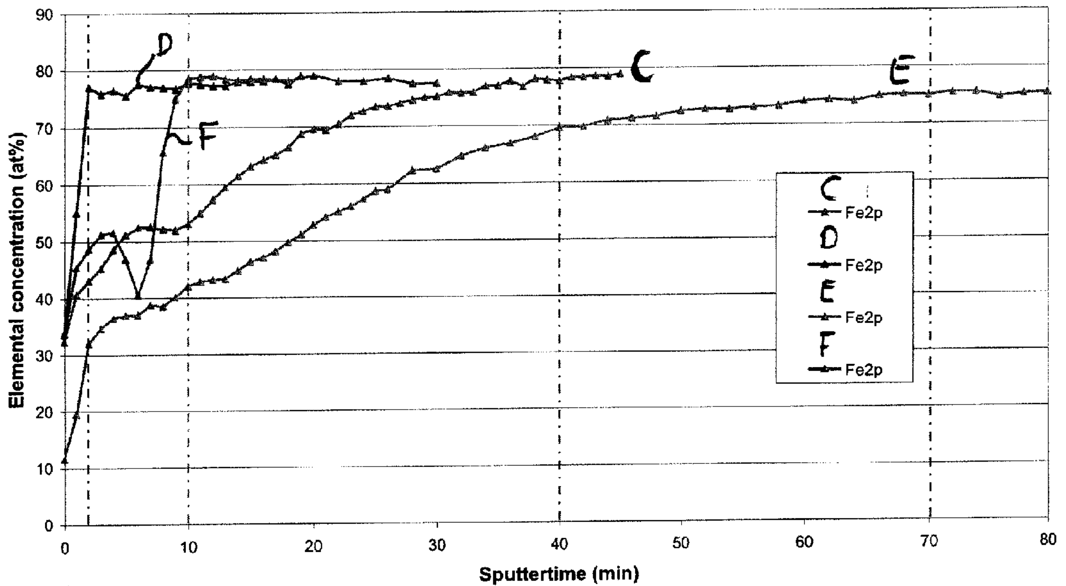


Fig. 14a

Comparison of O in Samples C to E

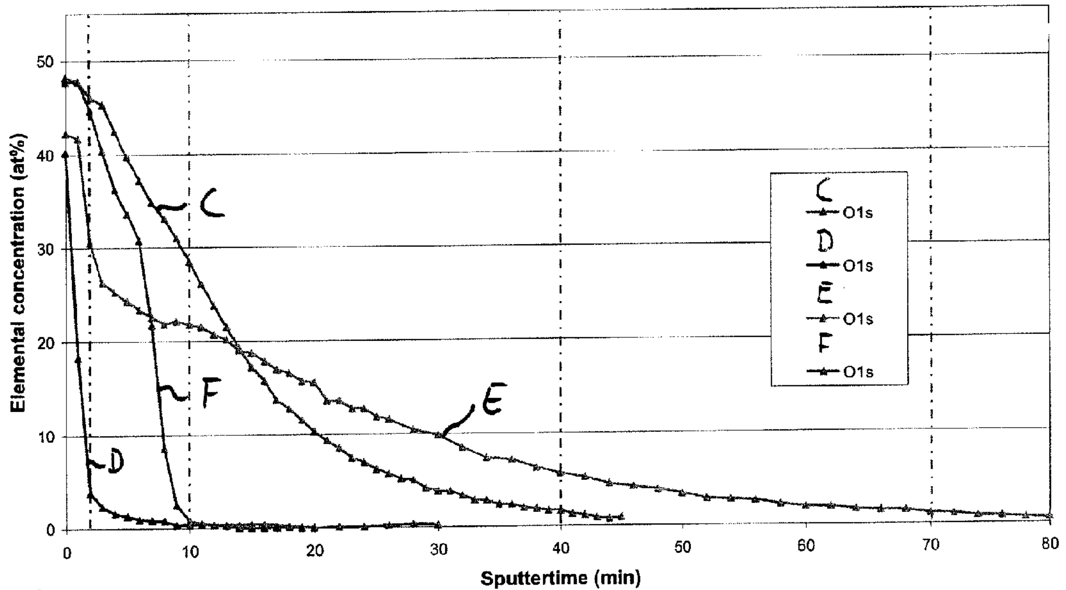


Fig. 14b

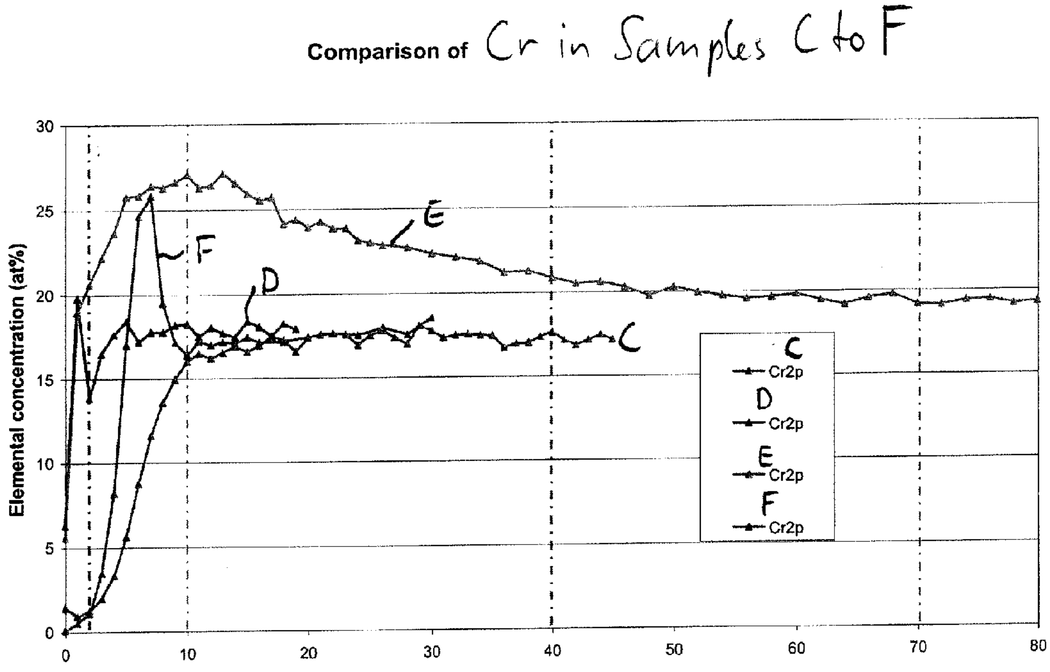

Comparison of Cr in Samples C to F

Fig. 14c

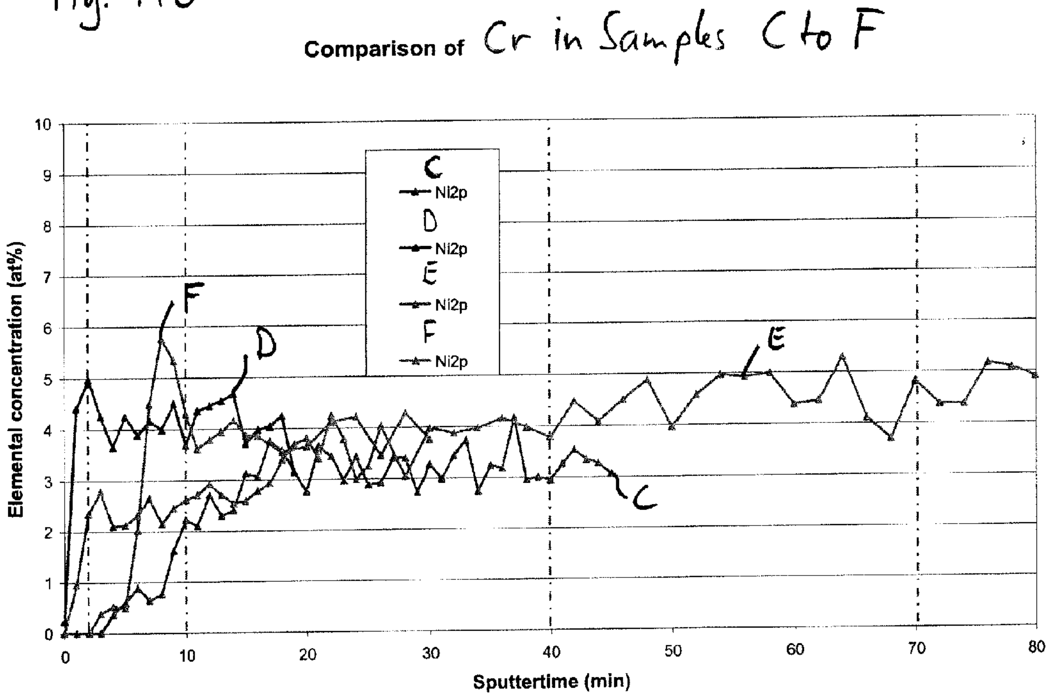

Comparison of Cr in Samples C to F

Fig. 14d

Comparison of Mn of Samples C to F

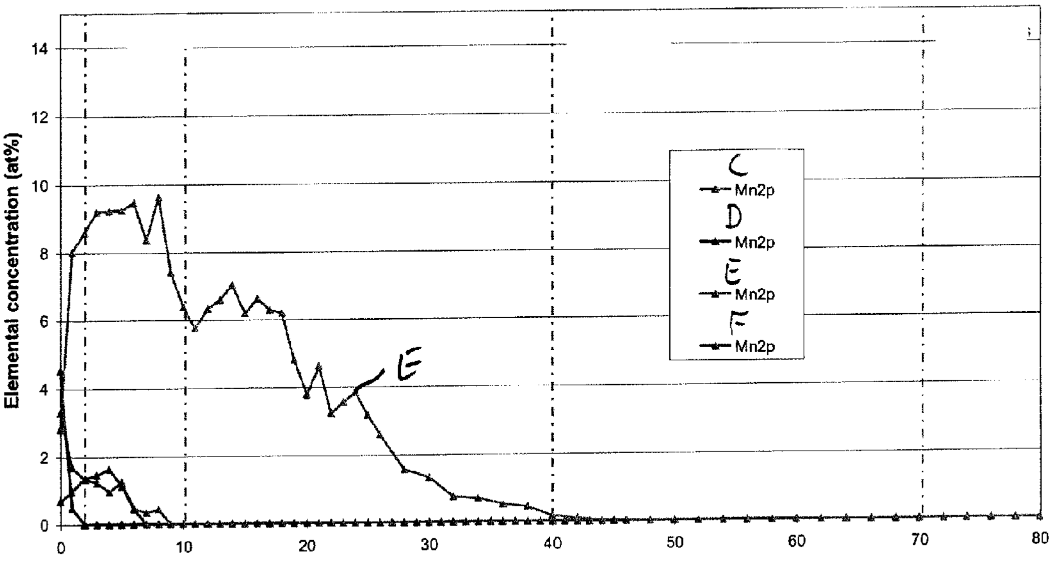


Fig. 14e

Comparison of depth profile band steel material

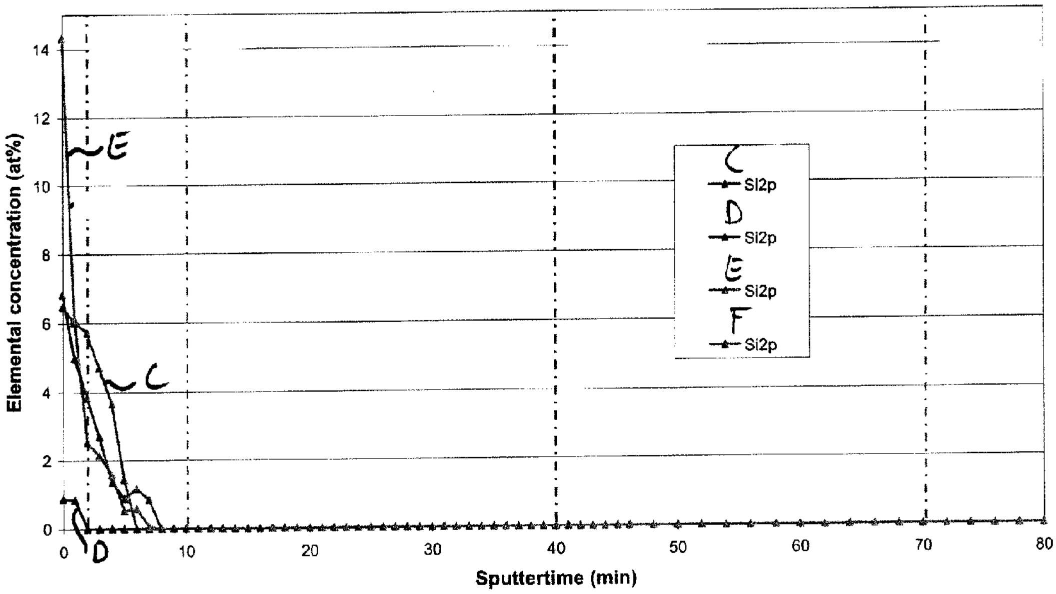


Fig. 14f

Sample C		Sputtertime [min]	C	O	Si	Fe	Cr	Mn	Ni	Pb	Cu
			Elemental concentration (at%)								
1.4310		0	6.8	48.2	6.5	32.3	1.4	3.3	-	0.5	1.0
		1	2.8	47.8	6.0	40.7	0.9	1.7	-	0.1	#
		2	2.6	46.1	5.7	43.0	1.3	1.3	-	#	-
		3	1.5	45.3	4.7	45.3	2.0	1.2	-	-	-
		4	0.7	42.5	3.7	48.6	3.3	1.0	0.4	-	-
		5	0.2	39.7	1.4	51.2	5.6	1.3	0.6	-	-
		6	0.2	37.2	-	52.5	8.8	0.5	0.9	-	-
		7	-	34.8	-	52.6	11.6	0.3	0.6	-	-
		8	-	33.1	-	52.2	13.6	0.4	0.8	-	-
		9	0.4	31.0	-	52.0	15.0	-	1.6	-	-
		10	0.2	28.5	-	53.1	16.0	-	2.2	-	-
		11	0.4	26.1	-	54.9	16.5	-	2.1	-	-
		12	-	23.8	-	57.3	16.2	-	2.7	-	-
		13	0.1	21.5	-	59.5	16.5	-	2.3	-	-
		15	-	17.2	-	63.1	16.6	-	3.1	-	-
		17	-	13.7	-	65.1	17.5	-	3.8	-	-
		19	-	11.5	-	68.8	16.6	-	3.2	-	-
		21	-	9.3	-	69.4	17.6	-	3.7	-	-
		23	-	7.5	-	72.0	17.6	-	3.0	-	-
		25	-	6.2	-	73.4	17.5	-	2.9	-	-
		27	-	5.2	-	74.0	17.4	-	3.4	-	-
		29	-	4.2	-	75.0	18.1	-	2.7	-	-
		31	-	3.8	-	75.9	17.4	-	3.0	-	-
		33	-	2.8	-	75.9	17.6	-	3.7	-	-
		35	-	2.3	-	77.0	17.5	-	3.2	-	-
		37	-	2.0	-	76.9	17.0	-	4.2	-	-
		39	-	1.7	-	77.9	17.4	-	3.0	-	-
		41	-	1.2	-	78.4	17.2	-	3.3	-	-
		43	-	0.9	-	78.7	17.2	-	3.3	-	-
		45	-	0.9	-	78.9	17.2	-	3.1	-	-

Fig. 15

- no detection possible
in traces (< 0.05 at%) detectable

Sample D		Sputtertime	Elemental concentration (at%)							
		[min]	C	O	Si	Fe	Cr	Mn	Ni	S
1.4301		0	13.5	40.2	0.9	33.6	6.3	4.5	0.2	0.8
		1	-	18.3	0.8	55.2	19.8	0.5	4.4	1.0
		2	0.4	3.8	-	77.1	13.9	-	5.0	-
		3	1.0	2.3	-	75.9	16.5	-	4.3	-
		4	0.6	1.6	-	76.5	17.7	-	3.7	-
		5	0.5	1.3	-	75.5	18.5	-	4.2	-
		6	0.5	0.9	-	77.6	17.2	-	3.9	-
		7	0.2	0.8	-	77.0	17.8	-	4.2	-
		8	0.5	0.8	-	76.9	17.8	-	4.0	-
		9	0.3	0.3	-	76.7	18.2	-	4.5	-
		10	-	0.3	-	77.7	18.3	-	3.7	-
		11	0.2	0.5	-	77.5	17.5	-	4.4	-
		12	-	0.3	-	77.2	18.1	-	4.5	-
		13	0.3	0.2	-	77.2	17.7	-	4.5	-
		14	-	-	-	77.8	17.5	-	4.7	-
		15	-	-	-	77.9	18.4	-	3.7	-
		16	-	-	-	77.9	18.1	-	4.0	-
		17	-	#	-	78.4	17.5	-	4.0	-
		18	-	0.1	-	77.4	18.3	-	4.3	-
		19	-	-	-	78.9	17.9	-	3.2	-

- no detection possible
in traces (< 0.05 at%) detectable

Fig. 16

Sample E		Sputtertime	Elemental concentration (at%)						
		[min]	C	O	Si	Fe	Cr	Mn	Ni
1.4301		0	23.4	42.3	14.3	11.6	5.6	2.8	-
		1	4.7	41.7	6.1	19.5	19.0	8.0	0.9
		2	3.3	30.6	2.5	32.0	20.6	8.6	2.4
		3	2.7	26.3	2.1	34.7	22.2	9.2	2.8
		4	1.7	25.3	1.6	36.5	23.6	9.2	2.1
		5	1.2	24.3	0.5	36.9	25.7	9.3	2.1
		6	1.4	23.4	0.6	37.0	25.8	9.5	2.3
		7	1.2	22.6	0.1	38.8	26.4	8.4	2.7
		8	1.6	21.9	-	38.5	26.3	9.7	2.1
		9	1.3	22.1	-	40.1	26.6	7.4	2.5
		10	0.1	21.8	-	42.1	27.0	6.4	2.6
		12	0.4	20.7	-	43.2	26.4	6.3	2.9
		14	0.2	19.0	-	44.8	26.5	7.0	2.5
		16	0.2	17.8	-	47.0	25.5	6.6	2.8
		18	-	16.6	-	49.7	24.1	6.2	3.4
		20	0.2	15.6	-	52.8	23.9	3.8	3.8
		22	-	13.6	-	55.1	23.8	3.2	4.2
		24	-	12.8	-	57.3	23.1	3.8	3.0
		26	-	11.6	-	59.0	22.8	2.6	4.0
		28	-	10.4	-	62.3	22.7	1.6	3.0
		30	-	9.8	-	62.5	22.3	1.3	4.0
		34	-	7.3	-	66.1	21.9	0.7	4.0
		38	-	6.3	-	68.0	21.3	0.4	4.0
		42	-	5.2	-	69.7	20.5	0.1	4.5
		46	-	4.2	-	71.0	20.3	-	4.5
		50	-	3.4	-	72.4	20.3	-	4.0
		54	-	2.7	-	72.6	19.8	-	5.0
		58	-	2.2	-	73.2	19.7	-	5.0
		62	-	1.8	-	74.2	19.5	-	4.5
		66	-	1.5	-	74.9	19.6	-	4.1
		70	-	1.1	-	74.9	19.2	-	4.8
		74	-	0.8	-	75.5	19.4	-	4.4
		78	-	0.6	-	75.1	19.2	-	5.1
		80	-	0.5	-	75.3	19.3	-	4.9

- no detection possible

Fig. 17

Sample F		Sputtertime [min]	Elemental concentration (at%)						
			C	O	Si	Fe	Cr	Mn	Ni
1.4310	113	0	10.9	47.7	6.8	33.8	0.1	0.7	-
		1	0.3	47.8	5.0	45.4	0.5	1.0	-
		2	0.4	44.6	3.8	48.7	1.1	1.4	-
		3	0.3	40.4	2.7	51.3	3.5	1.5	0.4
		4	0.3	36.3	1.4	51.7	8.2	1.6	0.5
		5	#	33.6	0.9	46.9	17.0	1.1	0.5
		6	0.6	30.8	1.2	40.5	24.6	0.4	2.0
		7	0.3	21.7	0.8	46.8	25.8	-	4.5
		8	0.5	8.6	-	65.7	19.5	-	5.8
		9	0.1	2.5	-	75.0	17.2	-	5.3
		10	-	0.8	-	78.6	16.4	-	4.3
		11	-	0.4	-	78.7	17.2	-	3.6
		12	0.1	0.3	-	78.9	17.0	-	3.8
		13	0.2	0.3	-	78.4	17.2	-	3.9
		14	0.3	0.3	-	78.2	17.1	-	4.2
		15	-	0.4	-	78.3	17.5	-	3.9
		16	0.3	0.3	-	78.4	17.2	-	3.9
		18	1.0	0.2	-	78.1	17.2	-	3.5
		20	-	-	-	78.9	17.5	-	3.6
		22	0.3	#	-	77.9	17.7	-	4.1
		24	0.2	0.1	-	77.9	17.6	-	4.2
		26	-	0.2	-	78.4	18.0	-	3.5
		28	0.4	0.3	-	77.4	17.6	-	4.3
		30	#	0.2	-	77.5	18.6	-	3.8

- no detection possible
in traces (< 0.05 at%) detectable

Fig. 18

Comparison of OXYGEN elemental concentrations of samples A, B, C, D, E, F

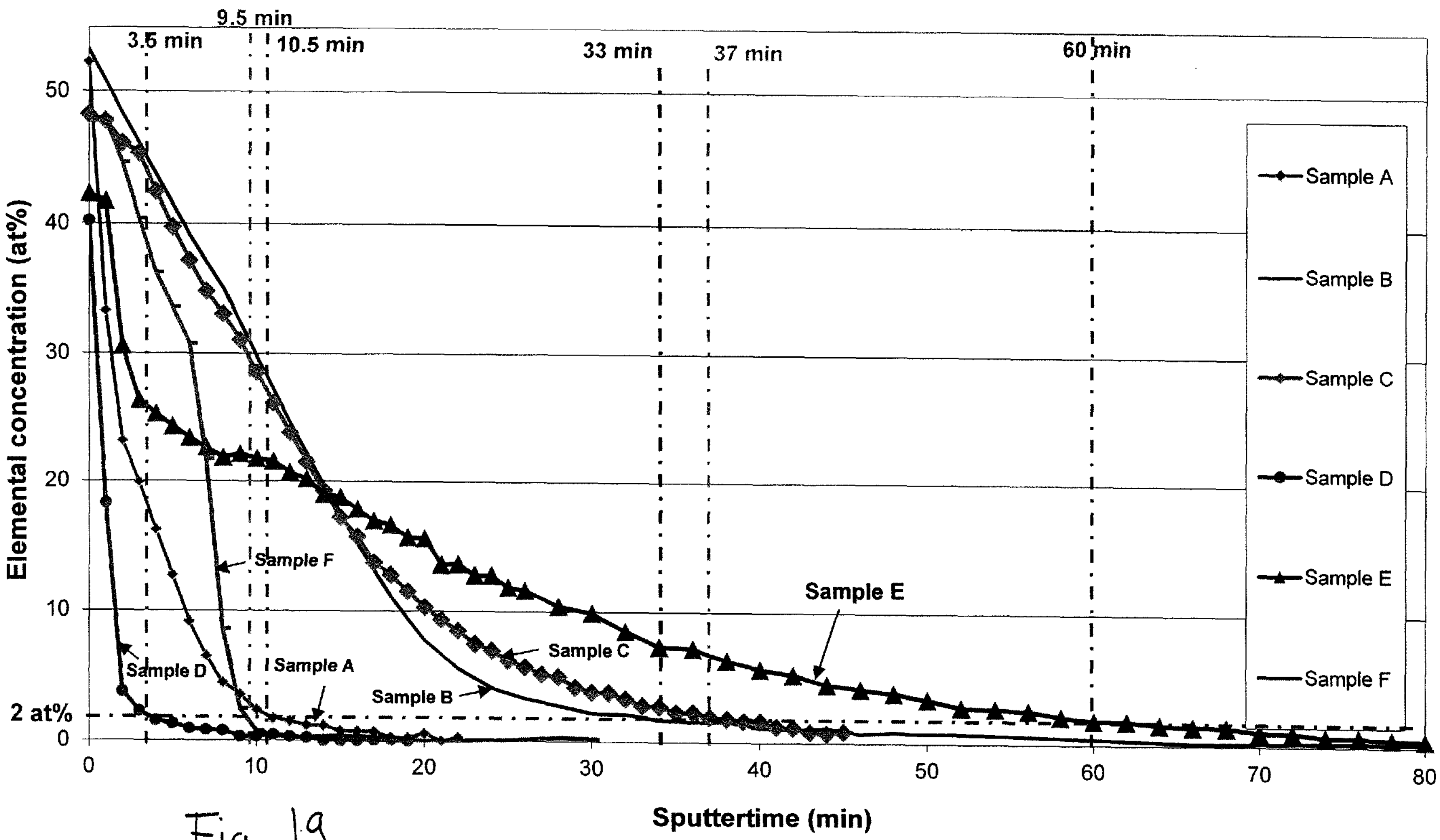


Fig. 1g

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EUROPEAN SEARCH REPORT

Application Number
EP 14 18 8695

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E06B
C22C

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	20 March 2015	Cobusneanu, D

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