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(54) **Wear resistant alloy**

(57) In order to provide a material of low cost that is suitable to produce parts or coatings having a high wear and also high chemical resistance, an alloy is propsoed comprising 13 to 16 percent by weight nickel (Ni), 13.5 to 16.5 percent by weight of chromium (Cr), 0.5 to 3 percent by weight of molybdenum (Mo), 3.5 to 4.5 percent by weight of silicon (Si), 3.5 to 4 percent by weight of boron (B) and 1.5 to 2.1 percent by weight of carbon (C), balance iron (Fe).

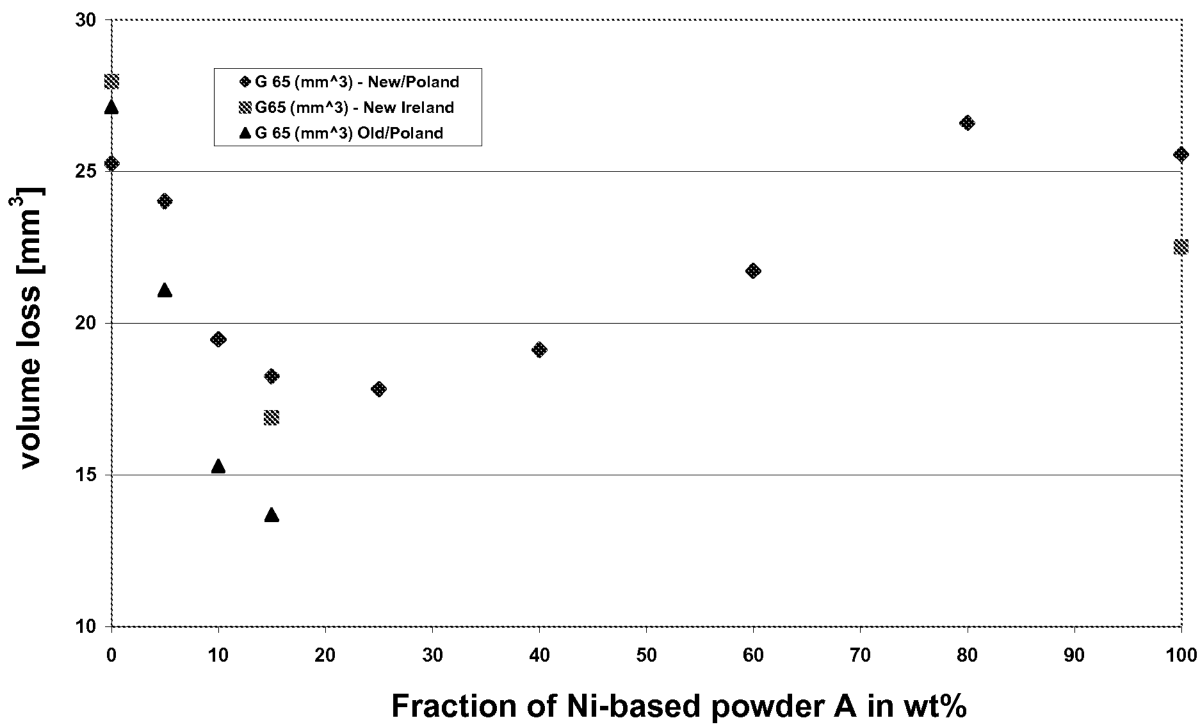


Fig. 1

EP 2 224 031 A1

Description

Detailed description

[0001] The invention relates to a material comprising an iron based alloy containing C, B, Cr, Ni, Si and Mo.

[0002] The material or alloy may be used for producing formed products, casted products, coatings, parts, coated parts, wires, electrodes, powders and powder mixtures.

Prior Art

[0003] There is a need in industry for an alloy material which has excellent resistance agains wear and corrosion and a low cost.

[0004] The use of nickel-based alloys with additions of chromium and molybdenum to give protection from wear and corrosion has long been known. Such alloys are disclosed for example in the patents US 6,027,583 A, US 6,187,115 A and US 6,322,857 A.

[0005] EP 1 788 104 A1 discloses a material for producing parts or coatings adapted for high wear and friction-intensive applications. The material comprises a nickel based alloy with the addition of hard particles such as WC.

[0006] The elements Ni and W are expensive and alternatives are sought.

[0007] Iron-based self-fluxing alloys are an alternative group of lower cost materials and many materials have been found that exhibit reasonable wear resistance.

[0008] Such an iron-based alloy is known from DE 197 33 306 C1. It discloses an iron-based thermal coating material. The alloy is used as additive material, in the form of a mixture, a gas atomized alloy, an agglomerated metal powder, a core-filled wire, a core-filled strip, a sintered strip or a cast sheathed rod electrode and used for thermal coating of components exposed to friction. A preferred composition of the alloy for applying a low friction and low wear layer for a sliding component pairing with good fatigue and impact resistance is as follows (by weight): 20-25% Mn, 13-20% Cr, 0.1-2% Ni, 3-6% W, 0.1-0.15% C, 1.5-2.5% B, balance Fe. Another preferred composition of the alloy for applying a low friction layer with high abrasion resistance and higher thermal loading capacity is as follows (by weight): 18-25% Mn, 13-25% Cr, 0.1-2% Ni, 3-5% W, 0.1-0.15% C, 4-6% B, balance Fe.

[0009] DE 199 01 170 A1 discloses another iron alloy with high carbon, boron, vanadium, chromium, molybdenum and nickel contents. The following composition is proposed (by weight): 2.0-4.0 % C, 2.0-4.5 % B, 0.5-3.5 % Si, 6.0-15.0 % Cr, 1.5-7.5 % Mo, 6.0-14.0 % V, 0-3.0 % W, 0-1.5 % Mn, 0-2.0 % Cu, 2.0-7.0 % Ni, balance Fe and impurities. The alloy is used for internal hard facing of metal cylinders by centrifugal casting or hot isostatic pressing.

[0010] CA 2 416 950 A1 discloses a material for the manufacture of parts and tools for use at elevated temperature, comprising an iron-based alloy comprising C, Si, Mn, Cr, Ni and N in certain concentrations. The alloy is cold formed to a hardness of at least 230 HB.

[0011] However, there remain two problems with such Fe-based alloys. First, the wear resistance of these Fe-based alloys is still inferior to Ni-based alloys with WC. To get close to those properties, the base alloy must use expensive alloying elements such as W, Nb or add large quantities of WC particles. These alloying elements increase the price and make the material very hard (more than 65 HRC), which poses additional processing and application problems with cracking. Secondly, the Fe-based materials do not have a good corrosion resistance, like that of Ni based alloys, particularly in mixed corrosion environments.

Object of the invention

[0012] It is therefore an object of the invention to provide an alternative material of lower cost that is suitable to produce parts or coatings having a high wear and also high chemical resistance.

[0013] The object is achieved by a material comprising an alloy containing 13 to 16 percent by weight nickel (Ni), 13.5 to 16.5 percent by weight of chromium (Cr), 0.5 to 3 percent by weight of molybdenum (Mo), 3.5 to 4.5 percent by weight of silicon (Si), 3.5 to 4 percent by weight of boron (B), 1.5 to 2.1 percent by weight of carbon (C) and 0.2 to 0.5 percent by weight of copper (Cu), balance iron (Fe).

[0014] It was found that such iron based alloys with C, B, Cr, Ni, Si and Mo exhibit high wear and surprisingly high chemical resistance.

[0015] The material comprises an iron based alloy with the further components C, B, Cr, Ni, Si and Mo. The material includes the pure alloy and coatings with a composition of the alloy.

[0016] The alloy contains only C, B, Cr, Ni, Si and Mo as major components besides the main component Fe. Generally the alloy contains traces or minor amounts of other elements, which are generally common impurities. Less preferred, the alloy may contain other elements in concentrations, which do not alter its chemical behavior significantly. Such optional additives are named accompanying elements.

[0017] The alloy is useful for producing either coatings on a metal substrate or for producing formed products, casted products, coatings, parts, coated parts, wires, electrodes or powders.

[0018] In general the alloy consists of 13 to 16 percent by weight (wt.-%) nickel (Ni), 13.5 to 16.5 percent by weight of chromium (Cr), 0.5 to 3 percent by weight of molybdenum (Mo), 3.5 to 4.5 percent by weight of silicon (Si), 3.5 to 4 percent by weight of boron (B) and 1.5 to 2.1 percent by weight of carbon (C)" balance iron (Fe) and possible impurities.

[0019] Impurities are normally present and are generally unavoidable. The content of impurities in the alloy is generally less than 1 percent by weight, preferably less than 0.5 percent by weight and most preferred less than 0.2 percent by weight. All weight percentages mentioned are based on the weight of the total composition, which is 100 percent by weight. All numerical values are approximate values.

[0020] In a less preferred alternative the alloy may contain one or more accompanying elements. The content of an accompanying element in the alloy is generally less than 3 percent by weight, preferably less than 2 percent by weight and most preferred less than 1 percent by weight. The whole content of accompanying elements in the alloy is generally less than 5 percent by weight, preferably less than 3 percent by weight and most preferred less than 2 percent by weight.

[0021] A preferred composition of the alloy is 13 to 14 percent by weight of nickel (Ni), 14 to 16 percent by weight of chromium (Cr), 1 to 3 percent by weight of molybdenum (Mo), 3.5 to 4.5 percent by weight of silicon (Si), 3.5 to 4 percent by weight of boron (B), 1.8 to 2.1 percent by weight of carbon (C) and 0.2 to 0.5 percent by weight of copper (Cu), balance iron (Fe) and possible impurities.

[0022] The alloy has an unusual good corrosion resistance in mixed corrosion conditions where most Ni-based or Fe-based wear resistant materials do not satisfy. It is remarkable that the Fe-based alloy contains no addition of other hard particles to increase its hardness, such as Tungsten Carbide (WC).

[0023] Generally the alloys have a hardness in the ränge of 35 HRC to 60 HRC, particularly in the range of 55 HRC to 60 HRC, typically around 58 HRC, which is unusually low for such a wear resistant material. It gives an advantage in processing and operation as it makes the alloy less sensitive to cracking.

[0024] Here, the unit "HR" represents the so called "Rockwell hardness". There are several Rockwell scales for different ranges of hardness. The most common are the B scale (HRB), which is appropriate for soft metals, and the C scale (HRC) for hard metals. The method for measuring hardness according to Rockwell is specified in DIN EN ISO 6508-ASTM E-18. Rockwell hardness numbers are not proportional to Vickers hardness readings, but there exist conversion tables, according to which the above range of 35 to 60 HRC is corresponding a Vickers hardness of between 345 and 780 HV/10.

[0025] The alloys generally have a melting point in the range of 1.000 to 1.150° C, typically around 1080° C. This a very low melting temperature for such an alloy with these properties, which reduces costs in processing and gives application advantages.

[0026] The alloy is produced in the conventional manner by melting of the components or blending of powders or compounds.

[0027] The alloy can be cast to products of any shape.

[0028] The alloy is used for the production of parts or coatings on parts, which are generally metal substrates or metal parts, especially made of steel. Metal parts are e.g. rotors, sleeves, bearings, screws, blades, etc.

[0029] The material, in particular the alloy, is preferably used for the production of wires, filling wires, bands, strand-shaped products, electrodes, powders, pastes, slurries, or cast bar material, which are used e.g. for casting, welding, plasma transferred arc welding (PTA), plasma powder build-up welding or arc welding, brazing, flame spraying, in particular high-speed flame spraying (HVOF), sinter fusing and similar processes.

[0030] The invention also comprises a process for applying a material according to the invention for the production of coatings with a high level of resistance to corrosion and wear on a workpiece by a thermal coating process, in which the coating material in powder form is alloyed and atomized from the melt or agglomerated from various alloyed and non-alloyed metal powders.

[0031] The coatings or protective layers of the alloy on parts, in particular metal parts, are produced preferably by conventional methods of applying a powder by pouring, casting, dipping, spraying, spinning followed by a thermal fusion treatment or by thermal methods like flame spraying, and preferably by high velocity flame spraying (HVOF), or by plasma transferred are welding. Such coating methods are described, for example, in US 6,187,115 A and US 6,322,857 A, which can be applied analogously and which are incorporated by reference.

[0032] Such coatings can be produced as mentioned above in the thermal processes by using materials containing the alloy, like powders, wires, electrodes or other conventional forms, or by applying two or more materials, which deviate in the composition from the resulting final alloy, where the materials are separate or mixed, e.g. different electrodes or mixed powders, resulting in a coating with the composition of the alloy.

[0033] Such coatings or protective layers serve to give protection from wear and corrosion in the chemical industry, the pharmaceutical industry, the paper industry, the glass industry, power industry, cement industry, waste and recycling, pulp and paper industry and the plastics-processing industry. Coated parts are also used advantageously for oil and gas exploration applications.

[0034] Generally the coating has a thickness in the range of 0.1 to 20 mm, preferably 1 to 10 mm.

Detailed description of preferred embodiments

[0035] The invention shall now be explained in more detail with reference to an embodiment and a drawing which shows in detail in

Fig. 1 a diagram on the degree of volume loss in a standardized abrasion testing (ASTM G65) in dependence upon the alloy composition,

Fig. 2 a diagram on the degree of weight loss in a standardized corrosion test in contact with HCl in dependence upon the Ni content of the X5 alloy; and

Fig. 3 a diagram on the degree of weight loss in a standardized corrosion test in contact with HNO_3 in dependence upon the Ni content of the X5 alloy.

Example 1 (Sample X5)

[0036] A series of alloys is prepared by the fusion of metal elements and compounds into a melt and producing two powders which are given in table 1 below:

Table 1

	Fe	**C**	**Si**	**Cr**	**Ni**	**Mo**	**B**
Powder A	3.7	0.26	4.58	16.4	59.76	12.9	2.87
Powder B	71.47	2.03	3.12	14.01	5.62	0	3.59

[0037] The Powder B (which is a Fe-based alloy) was blended with varying wt% of Powder A (which is a Ni based wear resistant alloy which is also designated by No. "53606") and then fused at 1.080 C. It was found that there was an optimal % of powder A for wear and corrosion results that lay between 10 and 40 weight % and that best results were obtained with 15% of Powder A **mixed** with Powder B

[0038] This illustrated in **Fig 1.** The 3 curves are wear rate data points obtained from the same fused mixtures but tested with the ASTM G65 method at three independent test series (different times and places). The volume loss is plotted on the y-axis in [mm^3] in dependence of the content of the Powder A in [wt%]. For all three test series a characteristical low volume loss and therefore best wear resistance were obtained with about 15% of Powder A mixed with Powder B.

[0039] In the following this 15% mixture of Powder A in Powder B alloy is called "X5". "X5" is a Fe-based alloy containing no addition of other hard particles to increase its hardness, such as Tungsten Carbide (WC). The following table 2 shows the composition of the X5 alloy in comparison with an Fe-based alloy as it is disclosed in DE 199 01 170 A1. It is obvious that the Ni-content of the X5-alloy is higher and its V-content is lower (namely zero) and the carbon and chrome levels are also different.

Table 2

	C	**Si**	**Cr**	**Ni**	**Mo**	**B**	**V**
X5	1.7	3.5	16.0	16.0	2.0	3.5	0
DE 199 01 170 **A1**	2.0-4.0	0.5-3.5	6.0-15	2.0-7.0	1.5-7.5	2.0-4.5	6.0-14.0

[0040] For both alloys: the balance is Fe (in the case of X5 the Fe balance is 57 wt%). The X5 alloy has a melting temperature of 1080° C. and low hardness of 58 HRC.

Wear test

[0041] In the ASTM G65 rubber wheel sand abrasion wear test the standard wear value of 13.68 mm^3 loss was recorded after 2000 revolutions of the wheel. This resulting wear resistant value is at a similar to the well established nickel-based wear resistant material called "12112", sold by Castolin Eutectic. This 12112 alloy is a blend of a NiCrBSi

12496 alloy matrix with 35% WC, which has the following composition:

Table 3

	Fe	C	Cr	B	Ni	Si	Mo
Alloy 12496 matrix	3.88	0.78	14.8	3.13	73.31	4.1	0

[0042] This Ni based 12112 alloy (= blend of alloy 12496 alloy with 35% WC) has been sold for at least 20 years and have been used to make Fused powder plates, sold under the name of CP 112, by Castolin Eutectic.

[0043] The fact that the Alloy X5 achieved the same G65 wear resistance result as the established 12112 is a surprise and a breakthrough, as the 12112 needs to have 35% of expensive WC added to achieve this value and an expensive Ni-based matrix. Alloy X5 is an Fe-based product and has no WC present.

Corrosion tests

[0044] For corrosion tests specimens with near cylindrical shape were prepared by melting of the test material in ceramic crucibles and cut into sliced with two exposed circular surfaces. The measurement of weight and surface area was recorded.

[0045] The test material are the above mentioned Fe-based powder B (table 1) and Ni-powders A (table 1, No. 53606) as well as powders of standard Ni-based alloys known as "12496" and "12497"(a slight chemical modification of alloy 12496). Said Ni-based powders were mixed with the Fe-based powder B (table 1) at various mixing ratios.

[0046] The slice specimens were exposed to HCl (33%), $HN0_3$ (55%), H_2SO_4 (96%) and acidic acid (80%) and the weight loss after 24h, 48h and 120h was measured. The corrosion resistance as specific weight loss (weight loss in mg per cm^2 and 24h) was determined.

[0047] The diagram of **Fig. 2** illustrates the corrosion test results of three test series for different compositions exposed to HCl (33%). The three curves are weight loss data points obtained from the corrosion tests as explained above. The weight loss is plotted on the y-axis in [mg/(cm^2 x h)] in dependence of the fraction of the respective Ni-based A powder of the mixed powders for the preparation of the specimens.

[0048] The diagram of **Fig. 3** illustrates the corrosion test results of three test series for different alloys exposed to $HN0_3$(55%).The three curves are weight loss data points obtained from the corrosion tests as explained above. The weight loss is plotted on the y-axis in [mg/(cm^2 x h)] in dependence of the content of the respective Ni-based A powder of the mixed powders for the preparation of the specimens.

[0049] The results are as follows:

- Ni-based alloys (A, 12496, 12497) show good corrosion resistance against HCl. Fe-based do not (Powder B). With increasing content of the Ni-based powder in the respective powder blends, the corrosion resistance against HCl increases.

- Fe-based alloy (B) shows good corrosion resistance against HNO_3. With increasing content of the Fe-based powder in the respective powder blends, the corrosion resistance against HNO_3 increases.

- Ni and Fe-based alloys are resistant against acetic acid and H_2SO_4.

- Adding Ni-based powders (A, 12496, 12497) to Powder B improves the corrosion resistance against HCl but decreases the resistance against HNO_3. The best balance is achieved with a Ni-based powder percentage of 5-15% as can be seen in Figs. 2 and 3.

[0050] The optimum alloy blend of Ni-based powder into the Fe-based Powder B composition is 15% (in wt% of the Ni-based powder) for HCl and HNO_3, with the use of Powder A as the best source of Ni-based alloy. This 15% / 85% mix gives the composition of X5 according to this preferred embodiment of the invention. This X5 composition also gives the lowest G65 wear resistance results.

Claims

1. A material comprising an alloy containing 13 to 16 percent by weight nickel (Ni), 13.5 to 16.5 percent by weight of chromium (Cr), 0.5 to 3 percent by weight of molybdenum (Mo), 3.5 to 4.5 percent by weight of silicon (Si), 3.5 to

4 percent by weight of boron (B) and 1.5 to 2.1 percent by weight of carbon (C), balance iron (Fe).

2. A material according to claim 1, wherein the alloy contains no other elements except impurities.

3. A material according to claim 1 or claim 2, wherein the alloy has a composition of 13 to 14 percent by weight of nickel (Ni), 14 to 16 percent by weight of chromium (Cr), 1 to 3 percent by weight of molybdenum (Mo), 3.5 to 4.5 percent by weight of silicon (Si), 3.5 to 4 percent by weight of boron (B), 1.8 to 2.1 percent by weight of carbon (C) and 0.2 to 0.5 percent by weight of copper (Cu), balance iron (Fe).

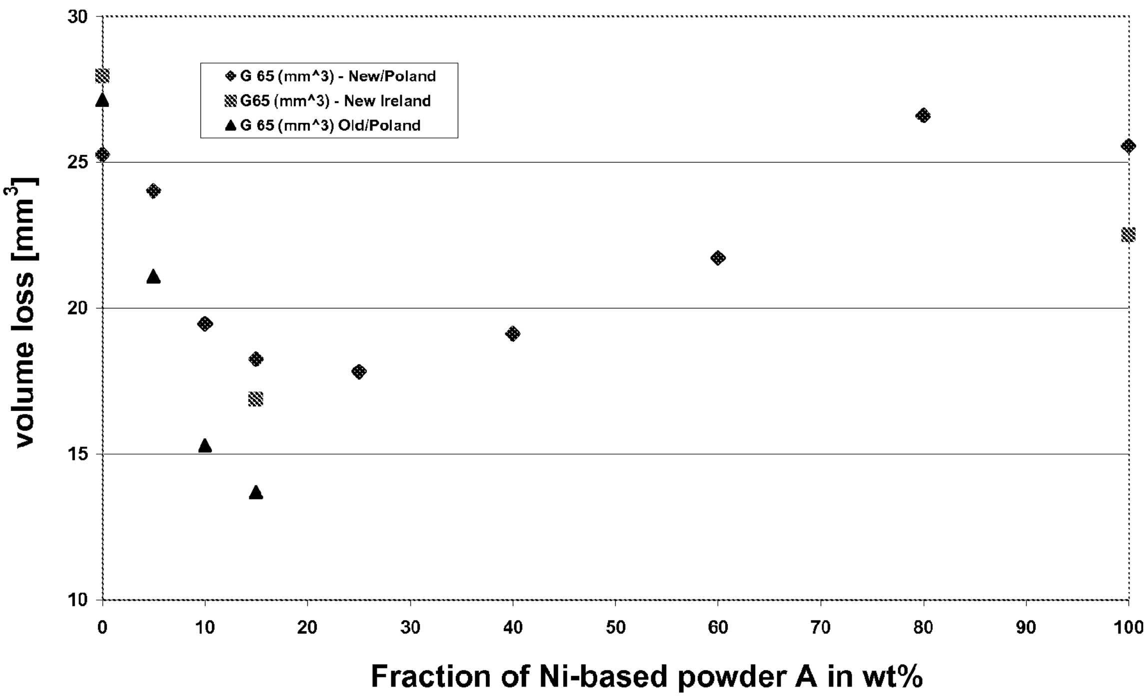
4. A material according to any of the preceding claims, wherein the alloy has a hardness of less than 60 HRC.

5. A material according to any of the preceding claims, wherein the alloy has a melting point of less than 1150° C.

6. A material according to any of the preceding claims, wherein the alloy is a powder or wire or the alloy is a coating on a metal substrate.

7. A material according to any of the preceding claims, wherein the alloy is free from preformed hard particles, especially from tungsten carbide.

8. A material according to any of the preceding claims, wherein the alloy contains less than 1 percent of weight of vanadium, most preferred the alloy is free from vanadium.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20
15
10
volume loss [mm3]
G 65 (mm^3) - New/Poland
G65 (mm^3) - New Ireland
G 65 (mm^3) Old/Poland
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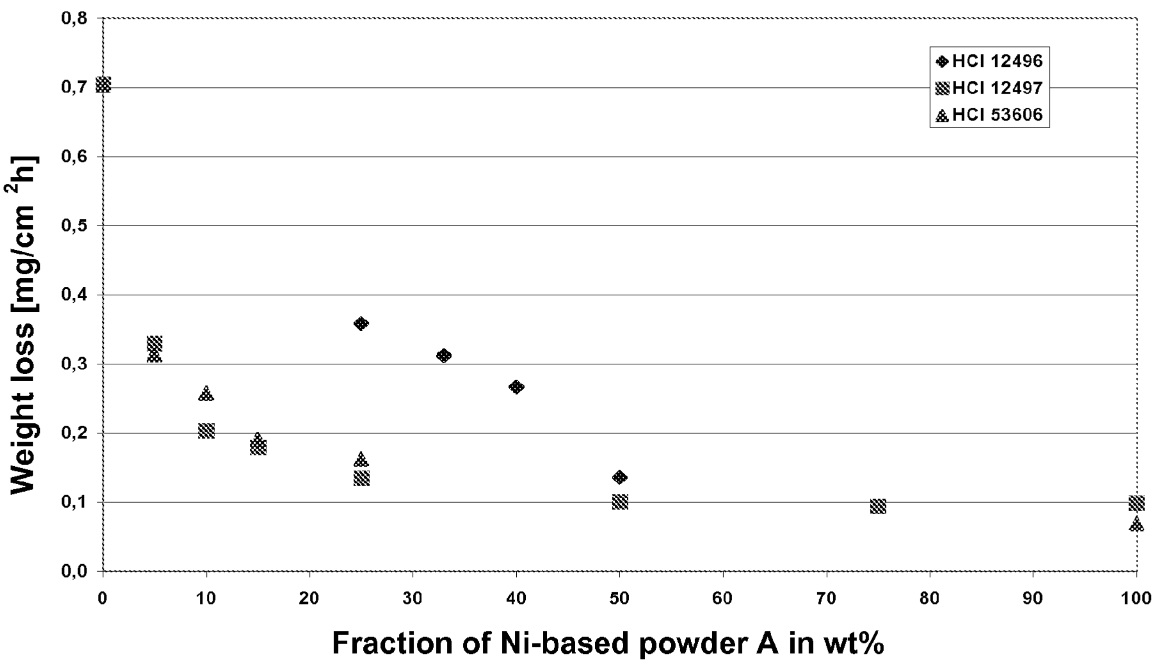
10
20
30
40
50
60
70
80
90
100
Fraction of Ni-based powder A in wt%

Fig. 1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0,5
0,4
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0,2
0,1
0,0
Weight loss [mg/cm 2h]
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HCl 12497
HCl 53606
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50
60
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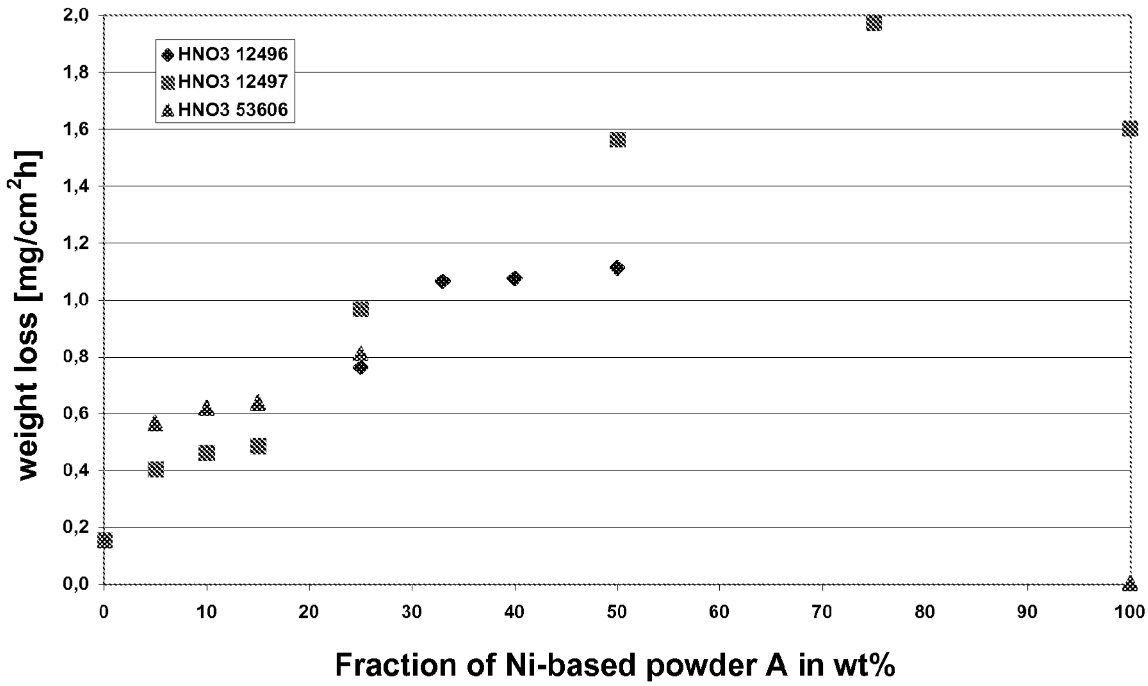
90
100
Fraction of Ni-based powder A in wt%

Fig. 2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1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0,0
weight loss [mg/cm²h]
HNO3 12496
HNO3 12497
HNO3 53606
0
10
20
30
40
50
60
70
80
90
100
Fraction of Ni-based powder A in wt%

Fig. 3

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EUROPEAN SEARCH REPORT

Application Number
EP 09 15 2975

DOCUMENTS CONSIDERED TO BE RELEVANT

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TECHNICAL FIELDS SEARCHED (IPC)

C22C
C23C
B22F

2

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	25 June 2009	Badcock, Gordon

CATEGORY OF CITED DOCUMENTS

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