



(43) International Publication Date
6 December 2012 (06.12.2012)

- (51) International Patent Classification:
H01H 1/02 (2006.01) *C22C 27/06* (2006.01)
C22C 1/04 (2006.01) *H01H 11/04* (2006.01)
- (21) International Application Number:
PCT/EP2012/002250
- (22) International Filing Date:
25 May 2012 (25.05.2012)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
11004375.9 27 May 2011 (27.05.2011) EP
- (71) Applicant (for all designated States except US): **ABB TECHNOLOGY AG** [CH/CH]; Affolternstrasse, 44, CH-8050 Zurich (CH).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **SIMON, Reinhard** [AT/CH]; Sommerhaldenstrasse 8, CH-5405 Dättwil (CH). **GENTSCH, Dietmar** [DE/DE]; Untere Steinhauser Strasse 26, 40882 Ratingen (DE).

- (74) Agent: **SCHMIDT, Karl-Michael**; ABB AG/GF-IPS, Oberhausener Straße 33, 40472 Ratingen (DE).
- (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, 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, 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, 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).

[Continued on next page]

(54) Title: CONTACT MATERIAL FOR VACUUMINTERRUPTER, AND METHOD OF MAKING A CONTACT MATERIAL

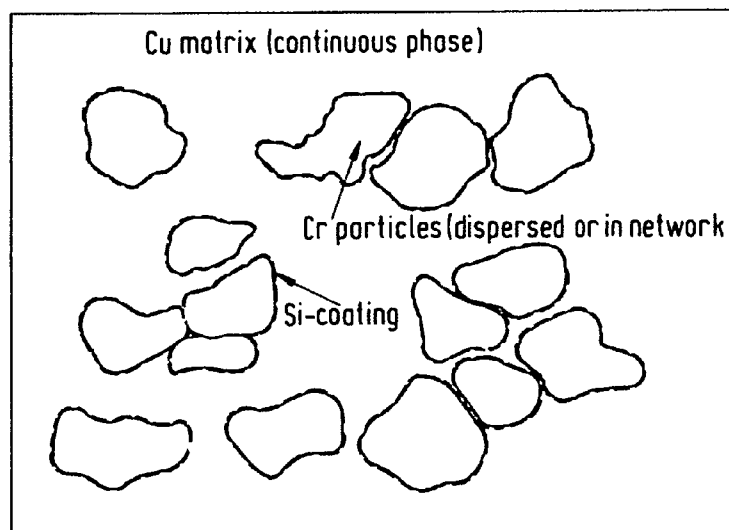


Fig.1

(57) Abstract: Contact material for vacuum interrupter, and method of making a contact material. In order to being enabled in a precise control of the Si concentration of Cu/Cr contact materials, contact material has a chromium content which is above 10 wt.% and that the material is doped with silicon below 0,2 wt.% (2000 ppm Si) and the remainder is copper Cu.

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

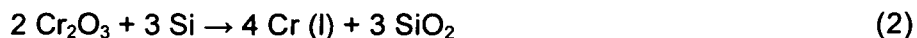
— *with international search report (Art. 21(3))*

5

Contact material for vacuuminterrupter, and method of making a contact material

10 Background of the invention

The predominant contact materials for vacuum interrupters are Cu/Cr composite materials consisting of typically 50 - 75 wt.% copper and 25 - 60 wt.% chromium. Conventional powder metallurgy techniques are mainly used for the production of these materials. It is well known from experience that the chemical composition of the contact material is very important for the application in vacuum interrupters. E.g. interstitial gas contents as well as copper-oxides and chromium-oxides should be kept as low as possible. In addition it was empirically found, that the Cu/Cr material should contain the element Si in a small quantity < 1 wt.% (more preferable < 0.2 wt.%) in order to achieve a high short-circuit current interruption performance of the vacuum interrupter. Alumino- or silicothermic produced Cr powders are widely used as today's main raw powder sources for the production of Cu/Cr materials. The alumino- or silicothermic method (also known as Goldschmidt-Process) is a comparable cheap technique used in the chromium metal industry. In this process the metals Al or Si or a mixture thereof is used to reduce Cr₂O₃ to Cr via the following reactions:



30 As a consequence of the reducing agents (Al or Si), Cr powder products contain residual contaminations of Si or/and Al in elemental and oxide form. The Cr is produced in batches in very big quantities (typical several tons each batch). In this rather rude technique a precise control of the Si contaminants is in practice impossible. As a consequence, there are rather high variations in local Si concentration within a

production batch and of course from batch to batch. This is a severe problem for the vacuum interrupter application, where a very precise control of the Si content at ppm-level is needed. It was found experimentally that variations in Si content of the contact material, which are related to different chromium batches, can lead to a very poor and random current interruption performance.

So it is the object of the invention, to solve the above described problem in a way that enables a precise control of the Si concentration of Cu/Cr contact materials.

Furthermore the Si is very homogeneously distributed within the contact material in order to generate the maximum doping effect. It results in a reliable performance of vacuum interrupters at very high level, which is independent of quality variations between different Cr raw powder batches.

Description of the invention

The problems are solved with the invention in that way, that the chromium content above is above 10 wt.% and that the material is doped with silicon below 0,2 wt.% (2000 ppm Si) and the remainder is copper Cu.

Further advantageous embodiment is, that the microstructure consists of chromium (Cr) particles which are covered by a thin layer of silicon (Si) or Si-based material (e.g. SiO_x).

Further advantageous is, that the silicon (Si) or Si-based material (e.g. SiO_x) is located at phase boundaries between chromium (Cr) and copper (Cu) and is therefore homogeneously distributed within the microstructure.

In detail, the unnotched impact bending strength of the material is higher than 30 J/cm².

Furthermore the electrical conductivity of the material is in the range of 30-35 MS/m.

For realizing that in a process of making the same, the chromium (Cr) particles are coated with a silicon-precursor, in order to bring in the silicon.

5 To introduce the silicon in a very effective way, the silicon-precursor is preferably a polysilazane or similar Si-containing polymer.

It is mostly advantageous, to use a powder metallurgical process for making the contact material in that way, that the coated Cr particles are further mixed with copper, pressed into contact shape, and finally sintered.

10 An advantageous use of a material according to at least one of claims 1 to 5, made by a process according to at least one of claims 6 to 8, is, that the material is used for contacts or contact surface coverage material for low, medium or high voltage switchgears.

15 A further advantageous use of it is for shielding, or shielding surface coverage material for medium or high voltage switchgears, especially in implementation in vacuum interrupters for medium voltage.

The invention is displayed in its functionality in the following figure and the description of the figures.

20

The invented material consists of chromium (Cr) particles either dispersed or arranged in a network within a continuous copper (Cu) matrix phase. Alternatively chromium (Cr) and copper (Cu) can also form an interpenetrating network of phases, depending on the content of chromium (Cr) and copper (Cu). The Cr particles or Cr phases are covered by a silicon (Si) based coating. A schematic drawing of the microstructure is shown in Figure 1. Although the overall Si content in the Cu/Cr material can be low, a homogeneous distribution of the Si dopant within the material microstructure is present resulting from the distribution of coated Cr particles. Figur 1 shows the microstructure of the invented copper/chromium (Cu/Cr) contact material. A homogeneous doping with silicon (Si) is realized by coating of chromium (Cr) particles by a Si-precursor. Figure 2 therefore shows a SEM micrograph of a Si-doped (280 ppm) and sintered Cu/Cr

25

30

material. The EDX linescan reveals Si at the Cr/Cr and Cr/Cu interfaces, which result from the coating of Cr particles by Si-precursor.

In Figure 2 a typical microstructure of Si-doped and sintered Cu/Cr contact material is given. The SEM micrograph reveals that Si is located as a coating on Cr particles. The Si can be clearly detected at Cr/Cr and Cr/Cu interfaces by a simple EDX linescan or any or any other appropriate technique. The Cr particles are well dispersed in the Cu matrix phase and in consequence the thin Si layers located at the Cr particle surfaces result in a homogeneous distribution of Si-dopant throughout the whole microstructure. It was found by the inventors that this kind of doping can affect the interface properties between Cr and Cu. The described Si-doped material exhibits an improved short-circuit current interruption as well as improved mechanical and electrical performance.

The problem of homogeneous distribution and precise control of Si dopant in Cu/Cr contact materials is solved by coating the Cr particles with a Si-precursor in a very simple wet-chemical process. In the described invention a polysilazane of the type PHPS (= perhydropolysilazane) was typically used as Si-precursor. In principle every type of polysilazane or other similar Si-containing precursor can be used to achieve the preferred Cu/Cr microstructure of the invented material. The coating causes a very homogeneous distribution of Si in the final Cu/Cr material, which is important to generate a maximum doping effect. Moreover by adjusting the Si-precursor concentration, a precise control of Si content of the final Cu/Cr material is easy to achieve. This guarantees a reliable performance of vacuum interrupters and a stable contact material production independent of raw powder variations.

The preferred PHPS precursor is purely inorganic. (Figure 3a) No carbon is included in the polymer structure. PHPS is readily soluble in non-polar organic solvents, like dibutylether, giving a transparent solution of very low viscosity (similar to water). The solvent is easily removable in air by evaporation. As already mentioned in principle every polysilazane or Si-containing precursor could be used. Nevertheless, for clarity of the invention the preferred precursor is specified in this document.

For the coating of Cr powders diluted precursor solutions can be made. Dibutylether is used as a solvent. The PHPS concentration in the precursor solution is typically in the

range of 0.5 – 1.5 wt.%. It can be easily adjusted to the target Si value of the final Cu/Cr material. By this a precise control of final Si-concentration in the ppm-range is achieved. For the coating process the Cr powder is simply immersed in the precursor solution. The precursor reacts immediately with the particle surface forming strong chemical (covalent) Si-O-Cr bonds. After a few minutes of mixing, the dibutylether is removed by evaporation. Most of the solvent is recovered in a condensation gap and can be reused. The resulting dry Cr powder particles are covered with a thin layer (few nm thick) of Si-precursor. Due to the fact that the drying step is performed in air, the Si-precursor layer on top of the Cr particle surface undergoes a slow cross-linking reaction which starts when the dried Cr powder comes in contact with air. The NH-groups of the PHPS react with moisture (H_2O) in the air to form Si-O-Si cross links and gaseous ammonia (see Figure 3b). The resulting coating on the Cr particles is transformed into a dense SiO_x layer. The Cr powder can be immediately mixed with Cu powder and subsequently pressed and sintered to a dense Cu/Cr contact material. Alternatively the coated Cr powder can also be stored and mixed with Cu powder to a later stage in order to continue the conventional powder metallurgy process by pressing and sintering to the final Cu/Cr contact material.

In Figure 4 a SEM micrographs of the uncoated and coated Cr powder are presented. The coated powder exhibits a very homogeneous Si distribution covering all surface area of the Cr particles. The colour code red expresses Si in the EDX mapping. XPS measurements revealed that the PHPS precursor was transformed during a full cross-linking reaction to a dense SiO_x layer, with x ranging from ~0.9 to ~1.1 on the outmost surface region (4 – 5 nm). After the full powder metallurgy processing to a sintered Cu/Cr contact material the Si concentration was measured by ICP-OES. The measured concentration of 280 ppm Si matched the target value of 290 ppm very well. (Figure 4b)

In the following, the main advantages of the invention are summarized briefly.

- Homogeneous and precisely controllable doping of Cu/Cr materials with Si forming a thin coating of Cr particles in the final microstructure.
- Homogeneous and precisely controllable doping of Cu/Cr materials with Si forming a thin coating of Cu particles in the final microstructure.

- Improvement of the current interruption performance of Cu/Cr contact materials and stable control of performance independent of variations in Cr raw powder quality.
- Improvement of the impact strength and fracture behaviour of Cu/Cr contact materials by strengthening of the Cu/Cr phase boundary.
- High electrical conductivity of the invented Si-doped contact material.

In order to demonstrate the fundamental different behaviors of undoped and Si-doped Cu/Cr contact materials, two typical examples for both types of material are given in the following. Both materials have been processed using the same raw powder source and almost identical processing steps. The only difference in processing was in the doping with Si. One was undoped (not coated with the Si precursor) and the other one was Si-doped (coated with the Si precursor). In order to evaluate the current interruption performance of contact materials, they are installed into commercial vacuum interrupters of the same design and tested under the same conditions. A standard three-phase electrical test procedure is performed to determine the limit in short-circuit current interruption ability.

In Figur 5 a graphical summary of the different observed interruption performance of undoped and Si-doped Cu/Cr materials is given. The red line in the graph marks the rated short circuit current of the used vacuum interrupter design. As can be seen, the undoped contact material is able to interrupt successfully the demanded value of 21 kA rms. However, interruption failure occurred at the next increased current step at 23.6 kA rms. The material offers no safety margin. In this case the interruption performance is very susceptible to small variations in Cr raw powder quality, which can lead to interruption failure already below the demanded rating.

In contrast, as can be seen clearly, the Si-doped material is able to interrupt much higher currents. A successful interruption at a current of 33.1 kA rms is observed. This is equal to a safety margin of 58% well above the demanded rating. This outstanding performance of Si-doped material qualities is based on their microstructure as shown in Figure 1 and Figure 2.

A further improvement of Cu/Cr contact materials is achieved with respect to their mechanical performance. Contacts for vacuum interrupters have to withstand

comparable high mechanical impact loads, because of the fast opening and closing speeds at which the interrupter is operated in service. It was found that Cu/Cr materials with Si-doping exhibit typically higher impact strengths compared with undoped materials. To give an example, in Figure 6, the impact strengths of two Cu/Cr materials are compared. Both materials have been processed using the same raw powder source and almost identical processing steps. The only difference in processing was in the doping with Si. One was undoped (not coated with the Si precursor) and the other one was Si-doped (coated with the Si precursor). The doped material shows a significant increase in impact strength.

This difference in mechanical performance can be explained by the accompanying fracture surfaces. Figure 7 shows fractographs of both materials in direct comparison. In the case of an undoped material, rather large gaps between Cr particles and the surrounding Cu phase are visible (see arrows in pictures), which reveal a rather poor bonding between both phases. In contrast, the Si-doped material shows an improved bonding between Cr particles and the Cu phase. This in turn leads to a pronounced trans-crystalline fracture of Cr particles.

Figure 7 (a) shows the fracture surface of undoped Cu/Cr contact material shows large gaps between Cr particles and Cu matrix phase (see yellow arrows in pictures). The bonding between Cr and Cu phase is comparable poor. In Figure 7 (b) The Si-doped Cu/Cr contact material exhibits an improved interfacial bonding between Cr and Cu phases. Therefore, trans-crystalline fracture of Cr particles is frequently observed (see green arrows in pictures).

Another important material property for the application in vacuum interrupters is the electrical conductivity of the contacts. In their major applications vacuum interrupters are operated in closed position most of the lifetime. A high electrical conductivity is of significant advantage in order to generate minimum losses under nominal currents. It is therefore important to note, that Si-doped Cu/Cr materials offer a comparable high electrical conductivity. This result was surprising, as usually almost all additives to copper based conductor materials lead basically to a decrease in electrical conductivity. However, the electrical conductivity of Si-doped Cu/Cr material (containing 280 ppm Si) is even higher than of the same undoped Cu/Cr material. Tab

1 summarizes the electrical conductivities of both materials, which have been processed almost identical. The only difference was in the doping with Si.

EXAMPLES

Example 1

A chromium raw powder batch with a measured (by ICP) Si content of 88 ppm was used as starting material. The target value of Si concentration in the final Cu/Cr contact material was set to be 290 ppm. A concentrated solution of 20 wt.% PHPS precursor was further diluted to 1.00 wt.% PHPS by addition of dibutylether. 1000 g of chromium powder was added to 128.0 g of the diluted precursor solution and mixed for a short period (< 30 min). After this the dispersion is dried by removal of the dibutylether solvent by rotational evaporation at a pressure of 40 mbar and a temperature of 60°C for approximately 1 hour. After this treatment the dry Cr powder was mixed with Cu powder in the ratio 25 wt.% Cr to 75 wt.% Cu. After pressing the Cu/Cr powder mixture and final sintering to a dense contact material the Si content was determined (by ICP) to be 280 ppm. The Si is homogeneously distributed within the sintered microstructure. The Si is typically located at the phase boundary between Cr and Cu.

Example 2

A chromium raw powder batch with a measured (by ICP) Si content of 52 ppm was used as starting material. The target value of Si concentration in the final Cu/Cr contact material was set to be 600 ppm. A concentrated solution of 20 wt.% PHPS precursor was further diluted to 1.40 wt.% PHPS by addition of dibutylether. 1000 g of chromium powder was added to 232.0 g of the diluted precursor solution and mixed for a short period (< 30 min). After this the dispersion is dried by removal of the dibutylether solvent by rotational evaporation at a pressure of 40 mbar and a temperature of 60°C for approximately 1.5 hours. After this treatment the dry Cr powder was mixed with Cu powder in the ratio 25 wt.% Cr to 75 wt.% Cu. After pressing the Cu/Cr powder mixture and final sintering to a dense contact material the Si content was determined (by ICP) to be 589 ppm. The Si is homogeneously distributed within the sintered microstructure. The Si is typically located at the phase boundary between Cr and Cu.

Contact material	Cu content [wt.%]	Cr content [wt.%]	Si content [ppm]	Electrical Conductivity [MS/m]
Cu/Cr without Si- doping	75	25	75	33.07
Cu/Cr with Si- doping	75	25	280	35.02

Tab 1

Claims

1. Contact material for vacuum interrupter with copper Cu and chromium Cr as contents,
5 **characterized in**
that the chromium content above is above 10 wt.% and that the material is doped with silicon below 0,2 wt.% (2000 ppm Si) and the remainder is copper Cu.
- 10 2. Contact material according to claim 1,
characterized in
that the microstructure consists of chromium (Cr) particles which are covered by a thin layer of silicon (Si) or Si-based material.
- 15 3. Contact material according to claim 1,
characterized in
that the microstructure consists of Copper (Cu) particles in fomr of Copper-powder, and the particles are covered with thin layers of Silicone (Si) or Si-based material.
- 20 4. Contact material according at least to claim 1, wherein the silicon (Si) or Si-based material is located at phase boundaries between chromium (Cr) and copper (Cu) and is therefore homogeneously distributed within the microstructure.
- 25 5. Contact material according at least to claim 1, wherein the Silicon or Si-based material is a mixture of coated Chromium and Copper powder.
- 30 6. Contact material according at least to claim 1, wherein the unnotched impact bending strength of the material is higher than 30 J/cm².

7. Contact material according at least to claim 1, wherein the electrical conductivity of the material is higher than 33 MS/m.

5

8. Contact material according at least to claim 1, wherein copper particles are coated with Si precursor.

9. Contact material according at least to claim 1, wherein both selected powders are coated with Si precursor.

10

10. Process for making the contact material according to one of claim 1 to 5, wherein chromium (Cr) particles are coated with a silicon-precursor.

11. Process for making the contact material according to claim 10, wherein the silicon-precursor is a polysilazane.

15

12. Process for making the contact material at least according to claim 8, or 9, or 10, or 11, characterized in that in a powder metallurgical process for making the contact material the coated Cr particles are further mixed with copper, pressed into contact shape, and finally sintered.

20

13. Use of a material according to at least one of claims 1 to 7, made by a process according to at least one of claims 6 to 8, characterized in that the material is used for contacts or contact surface coverage material for low, or medium or high voltage switchgears.

25

14. Use of a material according to at least one of claims 1 to 7, made by a process according to at least one of claims 8 to 12, characterized in that the material is used for shielding, or shielding surface coverage material for low, medium or high voltage switchgears.

30

15. Use of a material according to claim 14, characterized in that the material is implemented in vacuum interrupters for medium voltage.

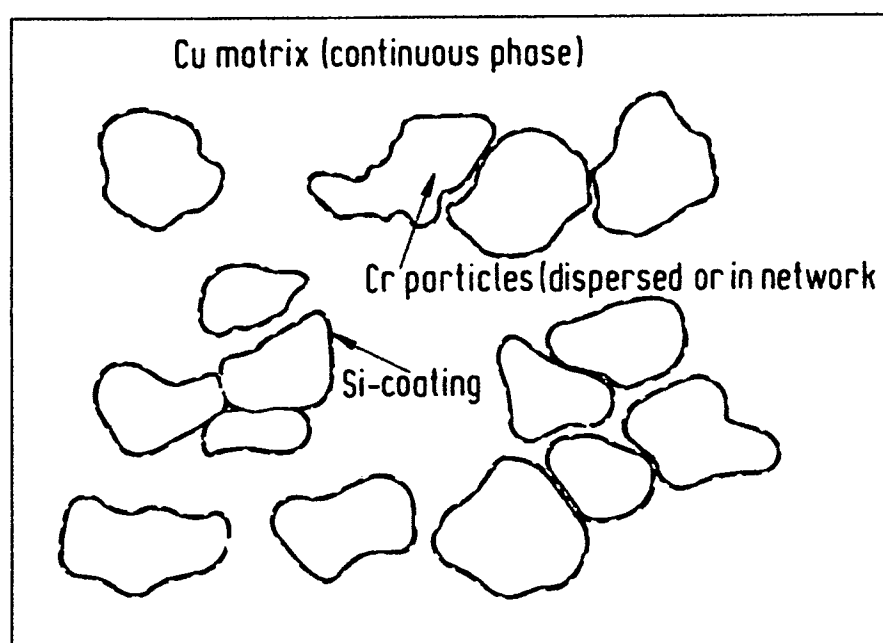


Fig.1

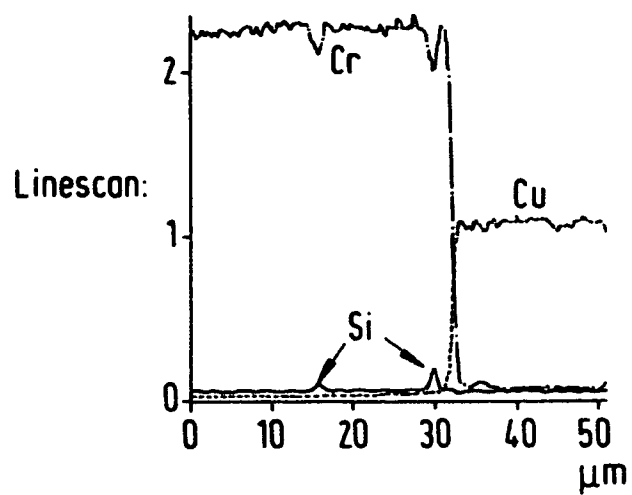
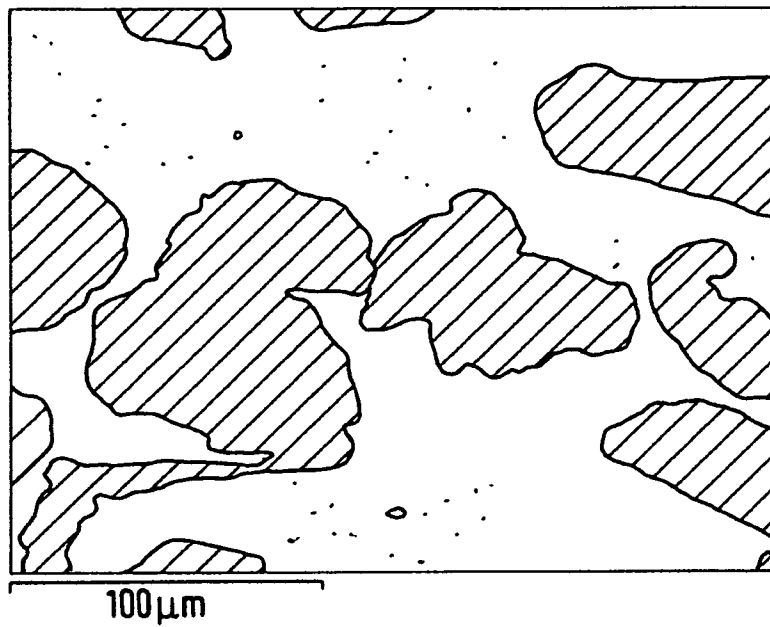


Fig.2

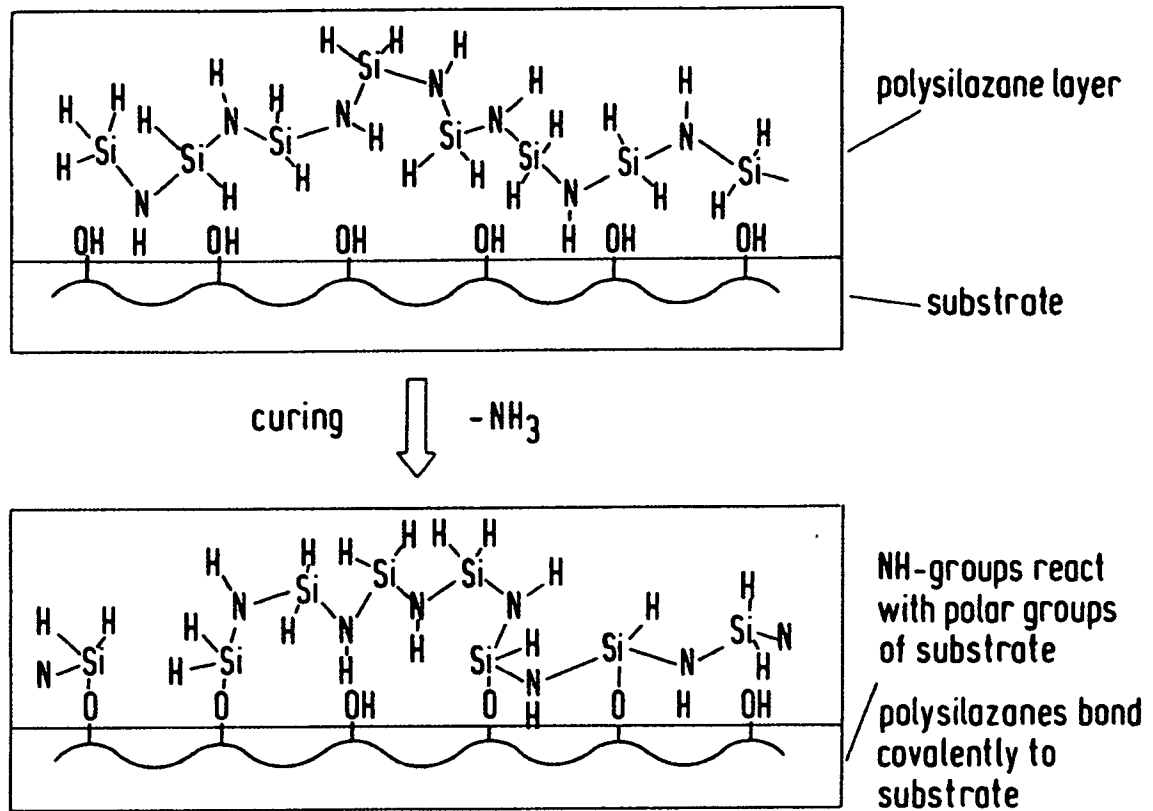


Fig.3a

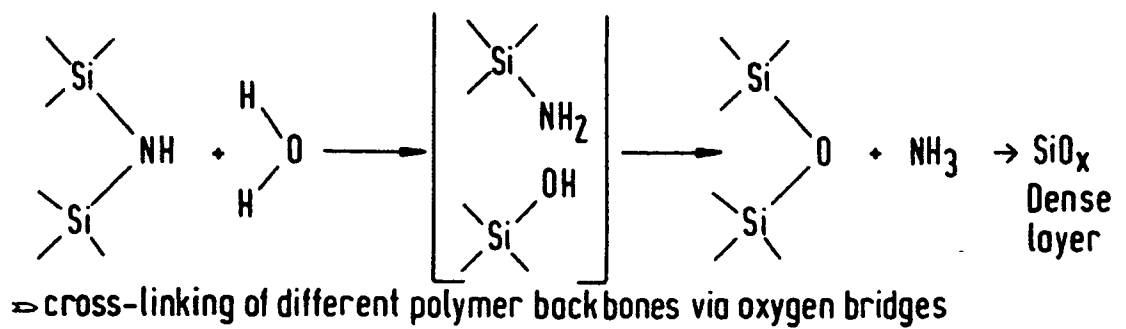
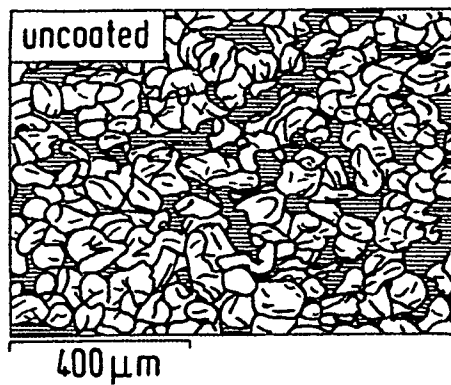


Fig.3b



Spectrum of EDX mapping

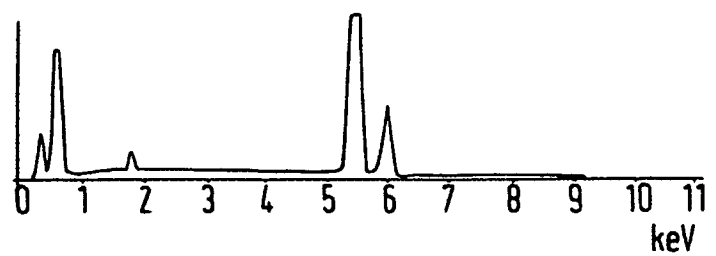
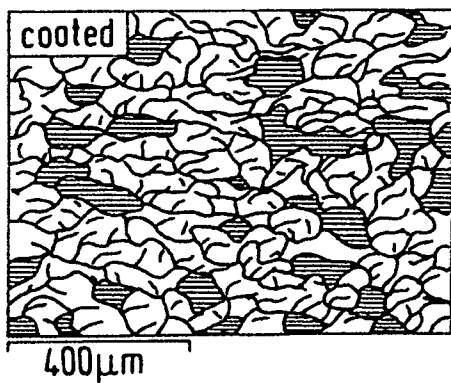


Fig.4a



ICP confirmed:

Precise doping of 280 ppm

XPS confirmed:

Cr particles are fully covered by a dense SiO_x layer

Si-distribution (EDX mapping)

Fig.4b

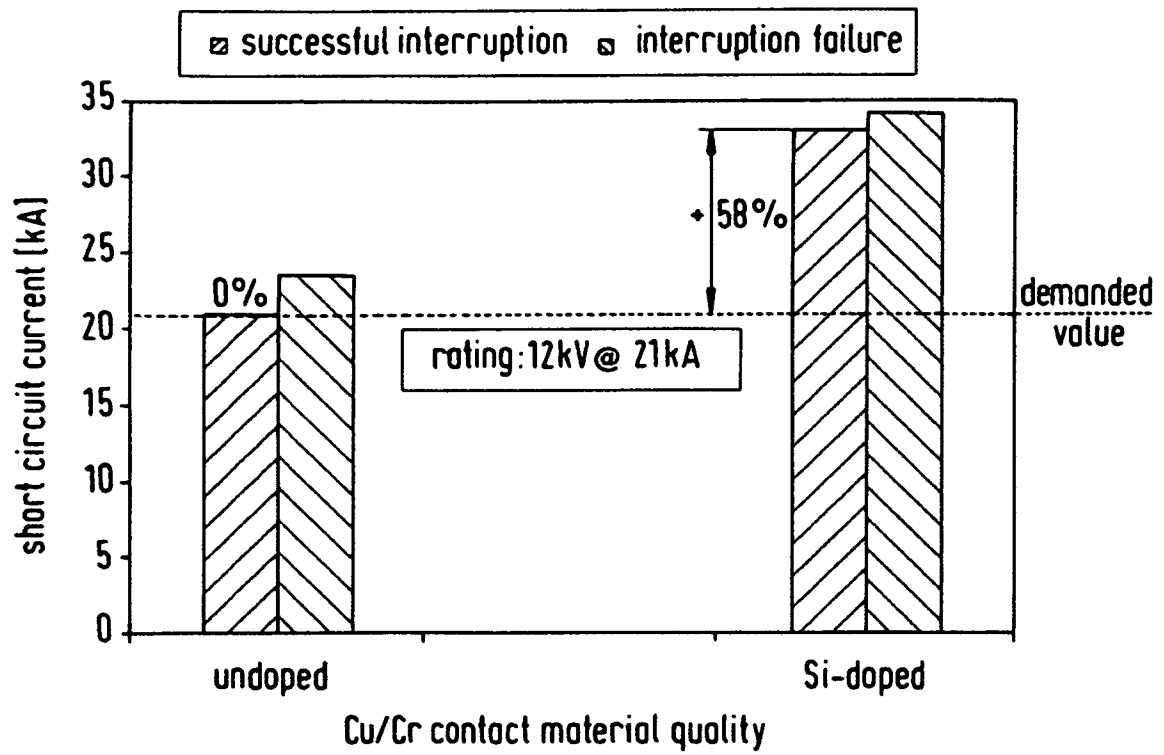
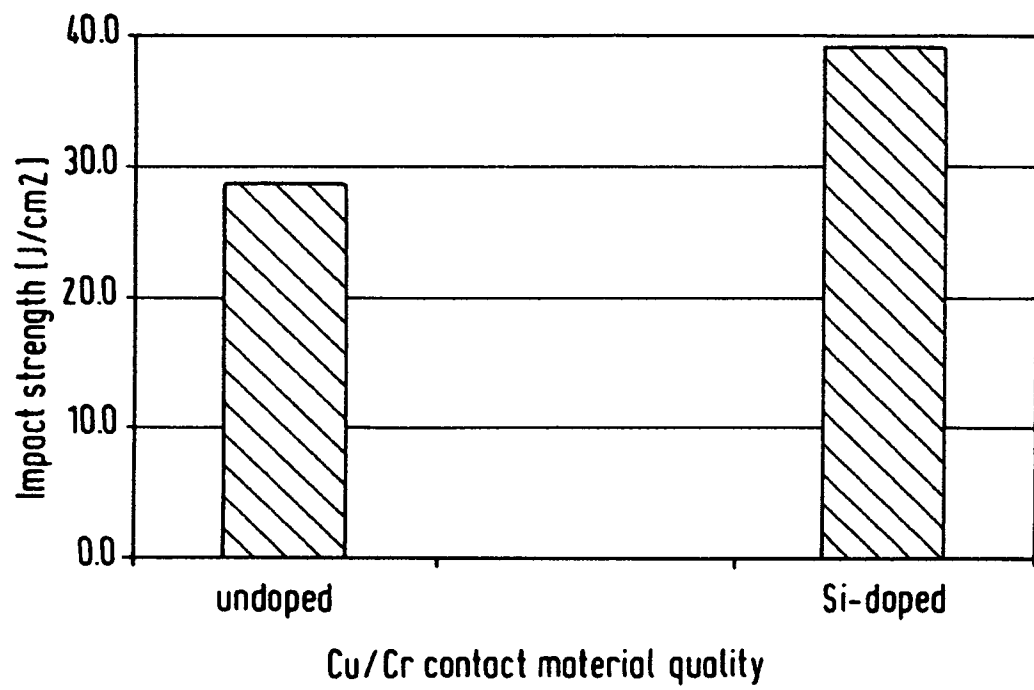


Fig.5

**Fig.6**

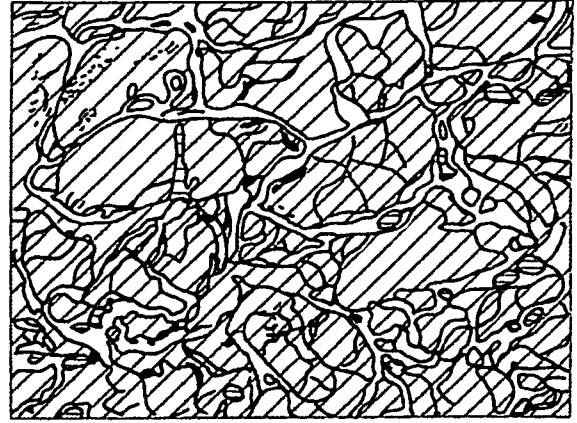


Fig.7a

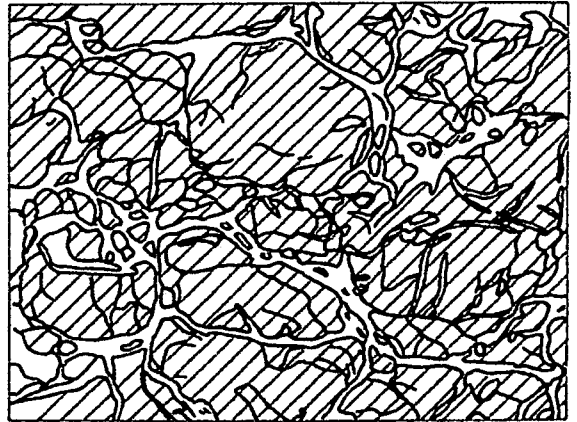


Fig.7b

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/002250

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01H1/02 C22C1/04 C22C27/06 H01H11/04
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)
H01H C22C

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 903 760 A2 (TOSHIBA KK [JP]) 24 March 1999 (1999-03-24) Embodiment 13; paragraph [0090]; figure 2 -----	1
X	EP 1 528 581 A1 (JAPAN AE POWER SYSTEMS CORP [JP]) 4 May 2005 (2005-05-04) abstract; claims 1-2 -----	1
X	US 2002/144977 A1 (KIKUCHI SHIGERU [JP] ET AL) 10 October 2002 (2002-10-10) paragraph [0053]; figure 1 -----	1



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"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

29 August 2012

Date of mailing of the international search report

05/09/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Glamán, C

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/002250

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0903760	A2	24-03-1999	CN 1213153 A 07-04-1999
			DE 69825227 D1 02-09-2004
			DE 69825227 T2 21-07-2005
			EP 0903760 A2 24-03-1999
			JP 3663038 B2 22-06-2005
			JP 11073830 A 16-03-1999
			US 6107582 A 22-08-2000

EP 1528581	A1	04-05-2005	CN 1612275 A 04-05-2005
			DE 602004008854 T2 19-06-2008
			EP 1528581 A1 04-05-2005
			JP 2005135778 A 26-05-2005
			US 2005092714 A1 05-05-2005

US 2002144977	A1	10-10-2002	JP 2002245907 A 30-08-2002
			US 2002144977 A1 10-10-2002
