(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 518 176 A2

(12) # EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
31.10.2012 Bulletin 2012/44

(21) Application number: **10839728.2**

(22) Date of filing: **20.12.2010**

(51) Int Cl.:
C22C 38/18 *(2006.01)* ***C22C 38/58*** *(2006.01)*

(86) International application number:
PCT/KR2010/009107

(87) International publication number:
WO 2011/078531 (30.06.2011 Gazette 2011/26)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **22.12.2009 KR 20090128883**

(71) Applicant: **Posco**
Gyeongsangbuk-do 790-704 (KR)

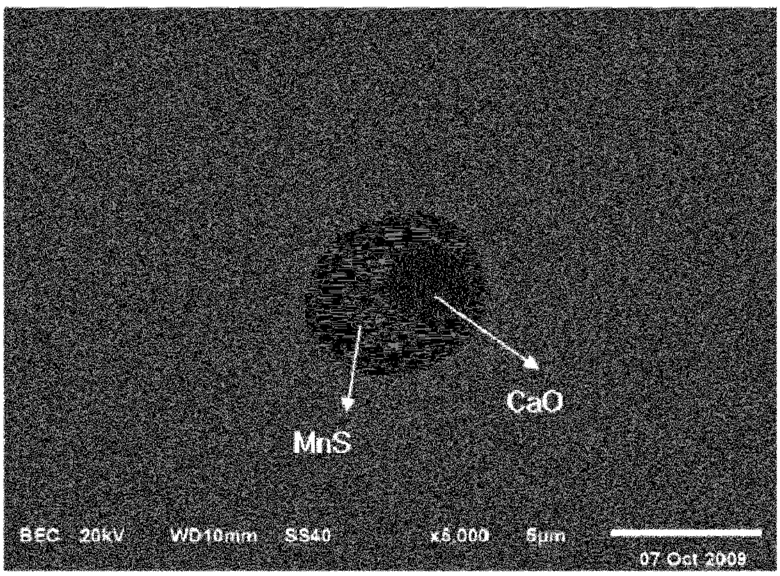
(72) Inventors:
- **JO, Ki-hoon**
Pohang-si
Gyeongsangbuk-do 790-704 (KR)
- **CHAE, Dong-chul**
Pohang-si
Gyeongsangbuk-do 790-704 (KR)
- **NAM, Chung-ho**
Pohang-si
Gyeongsangbuk-do 790-704 (KR)
- **KIM, Young-tae**
Pohang-si
Gyeongsangbuk-do 790-704 (KR)

(74) Representative: **Zech, Stefan Markus et al**
Meissner, Bolte & Partner GbR
Postfach 86 06 24
81633 München (DE)

(54) **MARTENSITE STAINLESS STEEL FOR AN INJECTION-MOULDING MOULD HAVING IMPROVED CORROSION RESISTANCE**

(57) Provided is a martensitic stainless steel for an injection-molding mold having outstanding machinability and corrosion resistance, which contains, as percentages by weight, 0.03 to 0.12% carbon, 0.02 to 0.08% nitrogen, 0.3 to 0.7% silicon, 0.6 to 2% manganese, 0.001 to 0.03% phosphorus, 0.1 to 0.3% sulfur, 11.5 to 15% chromium, 0.05 to 1% copper, 0.6 to 3% nickel and 0.0005 to 0.003% calcium, and iron and other unavoidable impurities as remnants.

[Fig. 1]



Printed by Jouve, 75001 PARIS (FR)

Description

[Technical Field]

[0001] An aspect of the present invention relates to a martensitic stainless steel for injection-molding mold having improved corrosion resistance, and more particularly, to a martensitic stainless steel used to produce an injection-molding mode or mode base.

[Background Art]

[0002] In general, as the amount of plastic used is increased, demands on plastic injection-molding machines have been rapidly increased. As the range and shape of plastic used is diversified, the kind of plastic injection-molding machine is diversified so as to satisfy such requirements. Accordingly, the kind and material of steel used 7in the plastic injection-molding machine is also developed to be suitable for its usage.

[0003] Conventionally, a high-hardness carbon steel containing high carbon was frequently used as a material for plastic injection-molding machines. However, since a stainless steel has high corrosion resistance, high durability according to its use for a long period of time and low thermal expansion coefficient under a high-temperature atmosphere, the use of the stainless steel has been gradually increased in recent years.

[0004] ASTM420 series stainless steel has been used as the stainless steel for producing components of the plastic injection-molding machine. However, since the hardness of the ASTM420 series stainless steel is high, it is not easy to perform mechanical processing. Since chromium carbide is formed through a reaction between chromium and carbon of a base material, the corrosion resistance is lowered, and the weldability is not satisfactory. For this reason, the use of the ASTM420 series stainless steel is gradually decreased.

[0005] In order to solve such problems, US Patent No. 6045633 has disclosed a stainless steel having improved corrosion resistance by limiting the content of carbon to 0.03 to 0.06% and adding 0.5 to 1.3% copper. However, it is difficult to secure sufficient corrosion resistance using such a method. In case where more than 1% copper is excessively added, the hot workability of the stainless steel is lowered, and therefore, surface cracks are caused.

[Disclosure of Invention]

[Technical Problem]

[0006] Accordingly, an object of the present invention is to provide an alloy design for improving the corrosion resistance and machinability of a martensitic stainless steel used as a material of a plastic injection-molding machine.

[Technical Solution]

[0007] According to an aspect of the present invention, there is provided a martensitic stainless steel for an injection-molding mold having improved corrosion resistance, which contains, as percentages by weight, 0.03 to 0.12% carbon, 0.02 to 0.08% nitrogen, 0.3 to 0.7% silicon, 0.6 to 2% manganese, 0.001 to 0.03% phosphorus, 0.1 to 0.3% sulfur, 11.5 to 15% chromium, 0.05 to 1% copper, 0.6 to 3% nickel and 0.0005 to 0.003% calcium, and iron and other unavoidable impurities as remnants.

[0008] The ratio of elongation to anisotropy of the stainless steel may be 0.5 or less, which is defined by the following formula,

[0009] Ratio of elongation to anisotropy = (rolling direction elongation - width direction elongation)/(rolling direction elongation).

[0010] The stainless steel may have a ferrite fraction of less than 15%. The hardness of the stainless steel may have a range of 25 to 40HRC.

[Advantageous Effects]

[0011] As described above, according to the present invention, it is possible to produce a martensitic stainless steel having outstanding corrosion resistance and improved anisotropy of machinability by increasing the content of nickel (Ni) while improving the distribution and structure of manganese sulfide (MnS) by adding calcium (Ca).

[Description of Drawings]

[0012]

FIG. 1 is a scanning electron microscope (SEM) photograph showing a structure of manganese sulfide (MnS) in a martensitic stainless steel having calcium (Ca) added thereto according to the present invention.
FIG. 2 is a graph showing a length distribution of MnS in a steel having no Ca added thereto as compared with the present invention.
FIG. 3 is a graph showing a length distribution of MnS in the martensitic stainless steel having Ca added thereto according to the present invention.
FIG. 4 is an SEM photograph showing a structure of a sample used in a corrosion test and a measurement method of a corrosion area.

[Mode for Carrying Out the Invention]

[0013] Hereinafter, preferred embodiments of the present invention will be described in detail with reference to the accompanying drawings. However, the present invention is not limited to the embodiments but may be implemented into different forms. These embodiments are provided only for illustrative purposes and for full understanding of the scope of the present invention by those skilled in the art. Throughout the drawings, like elements are designated by like reference numerals.
[0014] First, a martensitic stainless steel according to the present invention contains, as percentages by weight, 0.03 to 0.12% carbon, 0.02 to 0.08% nitrogen, 0.3 to 0.7% silicon, 0.6 to 2% manganese, 0.001 to 0.03% phosphorus, 0.1 to 0.3% sulfur, 11.5 to 15% chromium, 0.05 to 1% copper, 0.6 to 3% nickel and 0.0005 to 0.003% calcium, and iron and other unavoidable impurities as remnants.
[0015] Particularly, the present inventor has found that in the production of a steel used for a plastic injection-molding mold, the structure of manganese sulfide (MnS) existing in a martensitic cutting steel is improved by adding calcium (Ca), and the corrosion resistance of a base material is improved by adding nickel (Ni), so that the martensitic cutting steel has outstanding corrosion resistance.
[0016] Hereinafter, the function of the content of each composition and the reason for limiting its additional range will be described. In addition, percentages (%) described hereinbelow are all percentages by weight (wt%).
[0017] When the content of the carbon is low, the hardness of martensite is lowered, and hence the processing quality of the martensitic stainless steel is deteriorated. Therefore, more than 0.03% carbon is added. However, if the content of the carbon is excessive, the hardness of the martensite increases, and hence the productivity of the martensitic stainless steel is lowered. Since the excessive addition of the carbon lowers corrosion resistance, the maximum content of the carbon is limited to 0.12%.
[0018] Since the nitrogen contributes to the strength and corrosion resistance of the martensitic stainless steel, more than 0.02% nitrogen is added. However, if the nitrogen is excessively added, pores may be generated by the nitrogen in molding. Therefore, the maximum content of the nitrogen is limited to 0.08%.
[0019] Since the silicon is an element essentially added for the purpose of its deoxidation, more than 0.3% silicon is added. However, the silicon is excessively added, the machinability and thermal conductivity of the martensitic stainless steel are lowered. Therefore, the maximum content of the silicon is limited to 0.7%.
[0020] The manganese is an element added together with the sulfur so as to improve cuttability. When the content of the manganese is low, the added sulfur forms CrS or FeS, and hence has bad influence on workability. Therefore, more than 0.6% manganese is added. When the content of the manganese is 2% or more, its valid effect is lost. Therefore, the maximum content of the manganese is limited to 2%.
[0021] Since the phosphorus is an element unavoidably added in the production of stainless steel, more than 0.001% phosphorus is added. If the phosphorus is excessively added, the machinability of the martensitic stainless steel is lowered. Therefore, the maximum content of the phosphorus is limited to 0.03%.
[0022] Since the sulfur is a representative element added to improve the cuttability of stainless steel, more than 0.1% sulfur is added to secure the cuttability of the martensitic stainless steel. However, when the content of the sulfur exceeds 0.3%, the effect of the added sulfur is saturated, and the excessive addition of the sulfur lowers the workability of the martensitic stainless steel. Therefore, the maximum content of the sulfur is limited to 0.3%.
[0023] Since the chromium is a basic element for securing corrosion resistance, more than 11.5% chromium is added. However, when the chromium is excessively added, the chromium promotes the formation of ferrite. Therefore, the maximum content of the chromium is limited to 15%.
[0024] Since the copper functions to improve corrosion resistance and thermal conductivity, more than 0.05% copper is added. When the copper is excessively added, the copper causes the lowering of hot workability. Therefore, the maximum content of the copper is limited to 1%.
[0025] The nickel is an element that increases the corrosion resistance of stainless steel. Since the nickel functions to improve tension, more than 0.6% nickel is added. Therefore, the maximum content of the nickel is limited to 3% so as to prevent an excessive increase in production cost.
[0026] Since the calcium acts as a nuclear generation site of MnS in ingot casting or continuous casting, the MnS is

easily formed, and more than 0.0005% calcium is added to obtain an effect for suppressing the tension of Mn. When the calcium is excessively added, the calcium lowers corrosion resistance. Therefore, the maximum content of the calcium is limited to 0.003%.

[0027] Generally, a desired structure of the martensitic stainless steel is produced by making a casting slab through continuous casting or ingot casting and performing a rolling and forging process of the casting slab. Then, a heat treatment process using a unique method is performed to obtain an appropriate property of the steel suitable for its usage.

[0028] In the present invention, the ratio of elongation to anisotropy is preferably controlled to 0.5 or less. The ratio of elongation to anisotropy may be obtained by (rolling direction elongation - width direction elongation)/(rolling direction elongation). An ordinary steel for plastic injection-molding machine is not used by being machined to have a specific direction such as a rolling direction or width direction but used by being machined to have various directions. In this case, as the difference in mechanical property between directions increases, the deformation of the steel due to stress caused in the machining of the steel increases, and the difference in durability with respect to a high pressure applied in injection molding increases. The mechanical anisotropy [anisotropy ratio = (rolling direction experimental value - width direction experimental value)/(rolling direction experimental value)] is most obviously shown in the elongation among the several experimental values. Therefore, in steel having compositions of the inventive steel, the elongation anisotropy is preferably controlled to 50% or less.

[0029] Meanwhile, the inventive steel has the ideal structure of ferrite and martensite. The difference in hardness between the structures of the ferrite and the martensite is great. While the structure of the martensite has a solid and strong property, and the structure of the ferrite has a soft and tough property. When a small amount of ferrite exists in a material due to such a property, the ferrite functions to provide toughness. When an excessive of ferrite exists in the material, the ferrite functions to deteriorate workable quality. Therefore, in the material having compositions of the inventive steel, the maximum content of the ferrite is preferably limited to 15% or less.

[0030] The hardness of the inventive steel has a range of 25 to 40HRC. The hardness of an ordinary material has influence on machining quality and machinability (machining speed or tool lifetime) at the same time. If the hardness of the material increases, the resistance against machinability increases, and therefore, the machining speed decreases. Further, the abrasion of the tool increases, and therefore, the machinability is deteriorated. However, the quality of a machined surface is increased. On the other hand, if the hardness of the material is low, the machining speed and tool lifetime are increased, but the quality of the machined surface is lowered. Therefore, the hardness of the material is preferably 25HRC or more so as to secure the machining quality. The maximum hardness of the material is preferably less than 40HRC so as to secure the machinability in consideration of productivity.

(Embodiments)

[0031] For better understanding of the present invention, the present invention will be described through the following embodiments. In these embodiments, seven inventive steels and two comparative steels are produced by means of chemical formulae of Table 1. All samples are produced as ingots of 50Kg using a vacuum melting device and then rolled to a thickness of 25mm.

Table 1

Kind of Steel	C	Si	Mn	P	S	Cr	Ni	Cu	N	Ca
Inventive Steel 1	0.046	0.484	1.25	0.005	0.162	12.5	0.638	0.397	0.042	0.0008
Inventive Steel 2	0.101	0.492	1.03	0.006	0.135	16.08	2.72	1.00	0.069	0.0012
Inventive Steel 3	0.035	0.285	1.82	0.011	0.205	11.92	0.958	0.52	0.047	0.0021
Inventive Steel 4	0.046	0.477	1.21	0.007	0.076	13.00	1.58	0.2	0.026	0.0016
Inventive Steel 5	0.081	0.669	1.55	0.01	0.18	14.36	1.98	0.705	0.048	0.0011
Inventive Steel 6	0.053	0.411	1.25	0.006	0.155	12.22	1.31	0.331	0.513	0.0026
Inventive Steel 7	0.045	0.324	1.18	0.005	0.166	13.45	0.87	0.26	0.561	0.0017

(continued)

Kind of Steel	C	Si	Mn	P	S	Cr	Ni	Cu	N	Ca
Comparative Steel 1	0.05	0.321	1.27	0.02	0.151	12	-	-	0.052	-
Comparative Steel 2	0.087	0.221	1.5	0.003	0.11	12.1	0.03	0.434	0.044	-

[0032] In Table 1, calcium is not added to Comparative steels 1 and 2. Particularly, Comparative steel 1 is compared with the inventive steel in the state in which nickel and copper are not added to Comparative steel 1.

[0033] FIG. 1 is a scanning electron microscope (SEM) photograph showing a structure of MnS in an ingot sample having calcium added thereto. As can be seen in FIG. 1, calcium oxide is placed at a central portion of the MnS. In this case, the distribution of the MnS is detailed, and the elongation of the MnS is suppressed in a rolling process.

[0034] FIG. 2 is a graph showing a length distribution of MnS in Comparative steel 1 having no Ca added thereto. FIG. 3 shows a length distribution of MnS in Embodiment 7 of the inventive steel. As can be seen in FIGS. 2 and 3, in the steel having calcium added thereto, the number of coarse MnS is decreased by 20 or more as compared with the steel having no calcium added thereto. It can be seen that the average length and maximum length of the MnS are different from each other. Through the experimental result, it can be seen that when the calcium is added, the elongation of the MnS is limited to a certain degree in a rolling process. In case of the steel having MnS added thereto, the portion at which the MnS is added to the steel acts as a port weak to corrosion in a real use environment. When the elongation of the MnS is suppressed, it can be expected that the corrosion resistance will increase.

[0035] Meanwhile, in order to compare corrosions of samples, each of the samples was machined in the shape of a sheet of 150mm*70mm*1mm, and an experiment was performed in a complex corrosion environment of salt water spray, dry and humidity. The detailed experimental conditions are shown in Table 2. Table 3 shows a result obtained by performing experiments of corrosion resistance. After the experiments of corrosion resistance, the samples were estimated by dividing the corrosion grade into 1 to 10 according to a degree of formation of rust on the surface of the sample. '1' means that corrosion is formed in 50% of the area of the sample, and '10' means that rust is not formed at all.

Table 2

Test Name	Maintenance Time
Acidified Salt Mist Condition	2Hr
Dry Condition	4Hr
Wet Condition	2Hr

Table 3

Kind of Steel	Corrosion Grade
Inventive Steel 1	7
Inventive Steel 2	9
Inventive Steel 3	7
Inventive Steel 4	8
Inventive Steel 5	8
Inventive Steel 6	8
Inventive Steel 7	7
Comparative Steel 1	5
Comparative Steel 2	6

[0036] FIG. 4 illustrates samples of an embodiment used in the corrosion experiment and a comparative example having rust formed on the surface thereof. As can be seen in FIG. 4, the corrosion grade of the inventive steel having the compositions of the present invention is high. As shown in Table 3, it can be seen that the corrosion resistance of steel having a similar content of chromium having the most influence on the corrosion resistance of stainless steel is improved through the compositions of the present invention.

[0037] In the present invention, it can be seen that the addition of calcium has effective influence on the anisotropy of a mechanical property. When the MnS is elongated during a rolling process, the difference in mechanical property between the elongation direction of the MnS and the non-elongation direction of the MnS is great. This is because the MnS acts as a portion weak to an external force in the material. As the structure of the MnS for each direction is equalized, the anisotropy is decreased.

[0038] Table 4 shows a result obtained by measuring a mechanical property for each direction. It can be seen that the mechanical strength of stainless steel is increased by adding calcium. Particularly, the mechanical strength and elongation in the width direction are remarkably increased.

Table 4

Kind of Steel	Direction	TS (Mpa)	E1 (%)
Inventive Steel 7	Rolling Direction	1020	14
	Width Direction	1010	11
Comparative Steel 1	Rolling Direction	1000	14.5
	Width Direction	940	6

[0039] While the present invention has been described in connection with certain exemplary embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but, on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims, and equivalents thereof.

Claims

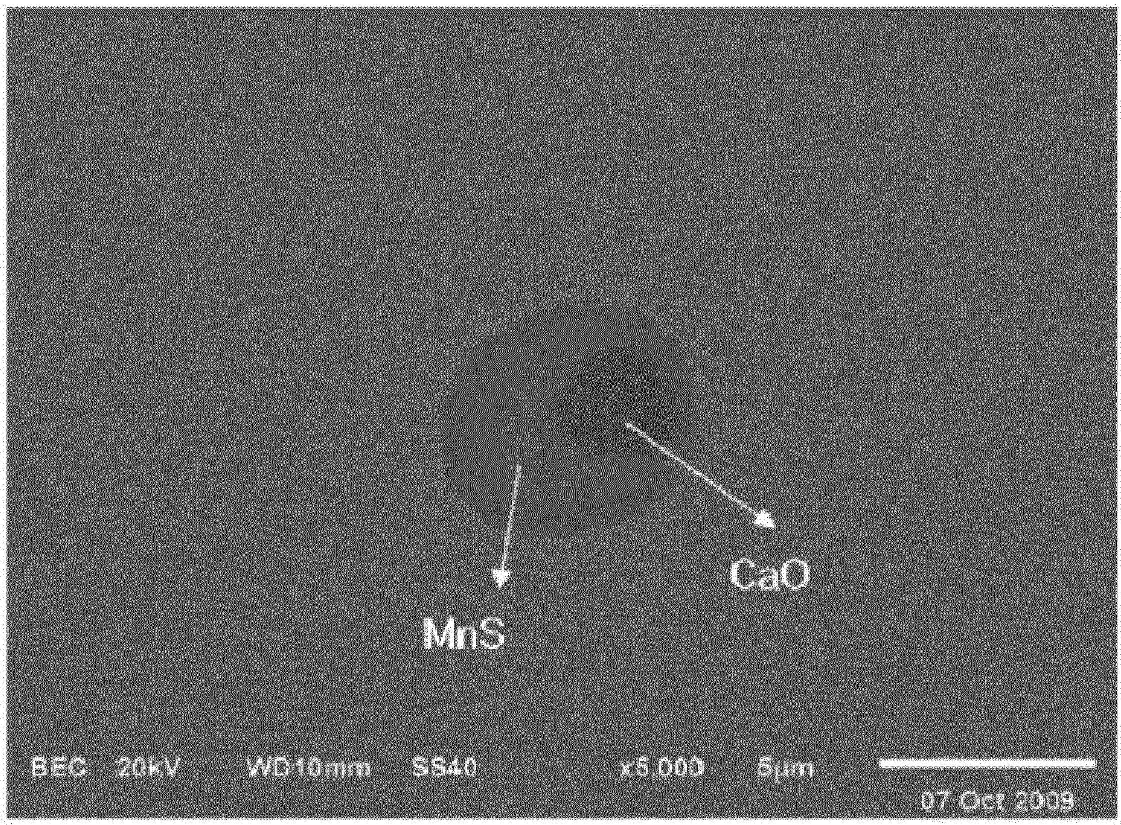
1. A martensitic stainless steel for an injection-molding mold having improved corrosion resistance, which contains, as percentages by weight, 0.03 to 0.12% carbon, 0.02 to 0.08% nitrogen, 0.3 to 0.7% silicon, 0.6 to 2% manganese, 0.001 to 0.03% phosphorus, 0.1 to 0.3% sulfur, 11.5 to 15% chromium, 0.05 to 1% copper, 0.6 to 3% nickel and 0.0005 to 0.003% calcium, and iron and other unavoidable impurities as remnants.

2. The martensitic stainless steel of claim 1, wherein the ratio of elongation to anisotropy of the stainless steel is 0.5 or less, which is defined by the following formula,
Ratio of elongation to anisotropy = (rolling direction elongation - width direction elongation)/(rolling direction elongation).

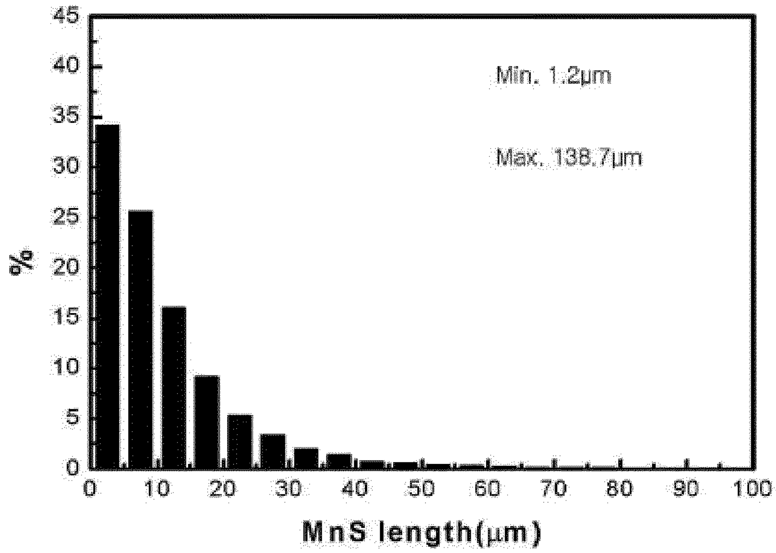
3. The martensitic stainless steel of claim 1, wherein the stainless steel has a ferrite fraction of less than 15%.

4. The martensitic stainless steel of claim 1, wherein the hardness of the stainless steel has a range of 25 to 40HRC.

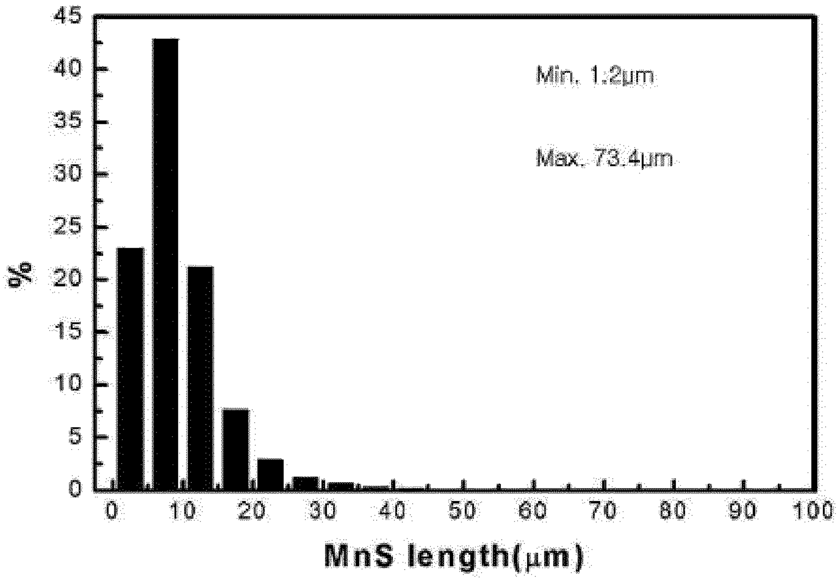
[Fig. 1]


MnS
CaO
BEC 20kV WD10mm SS40 x5,000 5μm
07 Oct 2009

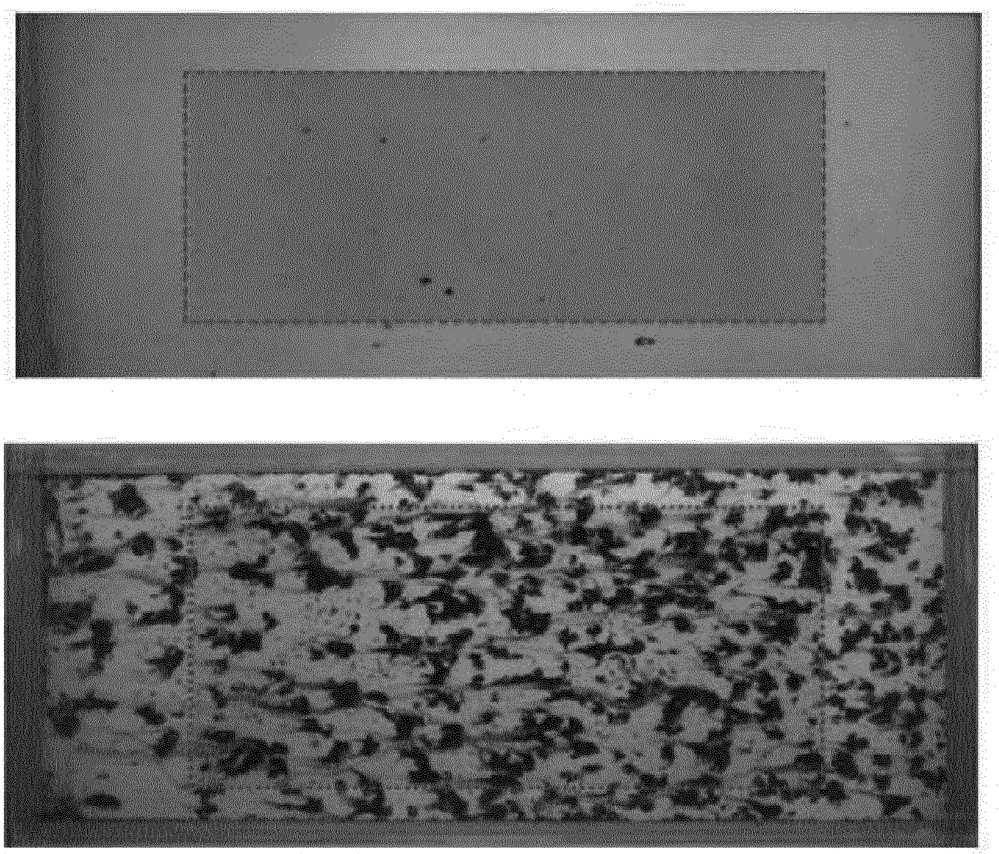
[Fig. 2]


Min. 1.2μm
Max. 138.7μm
%
MnS length(μm)
0 5 10 15 20 25 30 35 40 45
0 10 20 30 40 50 60 70 80 90 100

[Fig. 3]


Min. 1.2μm
Max. 73.4μm
%
0
5
10
15
20
25
30
35
40
45
0
10
20
30
40
50
60
70
80
90
100
MnS length(μm)

[Fig. 4]



REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 6045633 A **[0005]**