

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
30 September 2004 (30.09.2004)

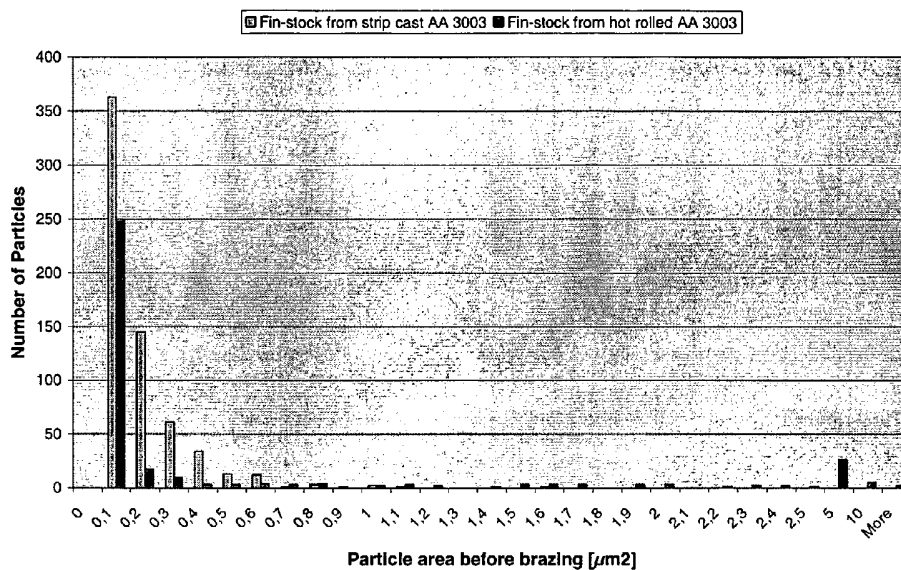
PCT

(10) International Publication Number
WO 2004/083473 A1

- (51) International Patent Classification⁷: C22C 21/00, C22F 1/04
- (74) Agent: BERG, André; Norsk Hydro ASA, N-0240 Oslo (NO).
- (21) International Application Number: PCT/NO2004/000074
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 19 March 2004 (19.03.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 20031276 19 March 2003 (19.03.2003) NO
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (for all designated States except US): NORSK HYDRO ASA [NO/NO]; N-0240 Oslo (NO).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): SYSLAK, Morten [NO/NO]; Stølsmyrv. 95, N-5542 Karmsund (NO). JIANG, Xiao-Jun [CN/NO]; Tujav. 13, N-5535 Hauge-sund (NO).

[Continued on next page]

(54) Title: A METHOD FOR PRODUCING ALUMINIUM ALLOY SHEET MATERIAL AND AN ALUMINIUM ALLOY SHEET



(57) Abstract: The invention relates to a method and an aluminium alloy sheet material. The method of producing aluminium alloy sheet material comprising the following steps: continuous strip casting of a sheet at a predetermined solidification rate ensuring material microstructure exhibiting primary particles having average size below 1 micrometer², and (cold) rolling of the strip cast sheet to an appropriate gauge with optionally intermediate annealing during the cold rolling. It is an object of the present invention to provide a novel method of production of Al-alloy sheets applicable on heat exchanger sheet based components resulting in improved pitting corrosion applying (base) Al-alloy material with higher Fe-content.

WO 2004/083473 A1



Published:

— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

"A method for producing aluminium alloy sheet material and an aluminium alloy sheet"

5 The present invention relates to a method of production of heat exchanger sheet based components and to components exhibiting improved pitting corrosion resistance provided by the method.

10 It is common practice to join aluminium components by disposing an aluminium brazing alloy between or adjacent to the component surfaces to be joined, and heating the brazing alloy and the joining surfaces in appropriately assembled fashion to a temperature (brazing temperature) at which the brazing alloy melts while the components remain unmelted. Upon subsequent cooling the brazing alloy forms a fillet or joint that bonds the joining surfaces of the components. For
15 assured selective melting of only the brazing alloy in the heating step, it is commonly preferred that the melting point of the brazing alloy be at least 30 to 40°C lower than that of the metal of the components. An example of a typical aluminium brazing alloy is an aluminium-silicon eutectic composition which starts to melt at about 577°C.

20

Aluminium rapidly forms a thin but tough and tenacious oxide film at room temperature, which thickens at elevated temperatures, inhibiting filler metal flow and wetting and therefore joint formation. All brazing processes are focused on the disruption or elimination of this undesirable oxide film at brazing temperatures. The
25 most common brazing methods for aluminium heat exchangers are vacuum brazing and controlled atmosphere brazing.

The vacuum technique relies on the addition of magnesium to the braze cladding material. Magnesium evaporates into the furnace vacuum at brazing temperatures and hence disrupts the overlying oxide film, allowing wetting and flowing of the
30 molten filler metal.

Controlled atmosphere brazing (CAB) relies on a flux to react with and remove the aluminium oxide. Fluoride-based fluxes, e.g. a mixture of potassium tetrafluoroaluminate and hexafluorotripotassium aluminate, are advantageous since they leave no corrosive residues.

5

The durability of a brazed aluminium heat exchanger in a corrosive environment is dependent on the inherent corrosion performance of each component (header, fin, tube) and their relative electrochemical behaviour. It is common practice to tailor the fin/fin-cladding and header/header-cladding in such a way that these components and the fillers become sacrificial to the tube. Furthermore, the inherent corrosion performance of each component is mainly described by the tendency and degree of pitting corrosion.

It is known that the severity of pitting corrosion in an aluminium alloy to some degree is dependent on the type of primary particle constituents and the relative electrochemical potential difference between particles and matrix. The electrochemical potential of primary particles is again dependent on the particle constituents. Iron (Fe) is a common impurity in aluminium alloys and present increase in degree of recycling of aluminium material results in relatively high iron contents. The solubility of Fe in aluminium is very low, in the order of 0.05% by weight at 655°C (Polmear 1). Thus, most of the Fe will be present in the form of particulate precipitates. The electrochemical potential of Fe is very cathodic compared to aluminium. It is known that the electrochemical potential of Fe-based Fe-bearing particles can be made more anodic by additions of e.g. manganese, and thus the potential difference between the aluminium matrix and the particles can be reduced. It has been demonstrated that such Mn additions have had an effect on improving the pitting corrosion of an aluminium alloy.

It has been found that the inherent corrosion performance expressed by the tendency for pitting corrosion is even more dependent on the physical size of the primary particle constituents. Whereas manganese additions aiming towards leveling of the corrosion potential have increased time to perforation in SWAAT

30

from 2-4 days to 6-8 days, controlling the particle size will give up from 20 days - indefinite life in SWAAT.

It is therefore an object of the present invention to provide a novel method of production of Al-alloy sheets applicable on heat exchanger sheet based components resulting in improved pitting corrosion applying (base) Al-alloy material with higher Fe-content.

This and other objects of the present invention are achieved by provision of a novel production method as claimed in the attached claim 1 and the resulting Al-alloy sheet in claim 7. Embodiments of the method is further defined in dependent claims 2 - 6, while further embodiments of the alloy sheet are defined in dependent claims 8 -11.

The invention will now be described in details as illustrated by way of examples and results from SWAAT tests conducted on Al-sheet samples provided by the novel production method compared to the reference samples as illustrated in the attached Figures 1-5, where

Fig. 1 shows a diagram of particle size distribution in the Al-sheets prior to brazing,

Fig. 2 is a corresponding diagram showing particle distribution after brazing,

Fig. 3 is a scanning electron microscopic image of the particles in the strip cast material according to the present invention after brazing, and

Fig. 4 is the reference scanning electron microscopic image of the particles in hot rolled material after brazing.

30

Fig. 5 is the simulated brazing cycle utilised for the testing materials.

The present production of aluminium sheets provided with a braze cladding material comprises steps of;

- casting of rolling ingot followed optionally by homogenizing,
- 5 - application of braze cladding material to ingot,
- preheating of rolling ingot to a range from 500 to 600°C,
- hot rolling of the clad ingot, and finally
- cold rolling to the specified gauge sheet.

10 In addition to low solidification rate, also the prolonged exposure of ingots to elevated temperatures during the hot rolling operation results in segregation of alloying elements, coarse primary particles and dispersoids. In particular this applies for the size of Fe-bearing primary particles being controlled by solidification rate.

15

According to the present invention an inherent characteristic of continuous strip casting process, namely cooling rate and thus solidification rate of the cast sheets being of several orders of magnitude higher compared to commercial DC cast and hot rolled ingot material, has been applied in the novel method of production.

20

The novel production process comprises steps of;

- continuous strip casting of an Al-alloy sheet at predetermined solidification rate, in a range from 10^2 to 10^3 °C/sec, and
- 25 - cold rolling of the cast sheet optionally followed by annealing.

In general, unclad fin material is applied to welded tube which is clad with Al-Si braze metal. After brazing, residual cladding will in some way protect the tube core from corrosion attack. By providing a flux retaining coating on the said
30 continuous cast sheet surface, especially if the flux is (reactive) fluoride-based flux, it is possible to utilize the improved corrosion resistance of continuous strip cast sheets in manufacturing of heat exchanger components with further improved

corrosion resistance. In this case, at least one of the flat surfaces of the said continuous cast sheet is coated with a reactive flux retaining coating capable of providing joints in a brazing process, characterized in that the flat surface at least partially is coated with a flux retaining composition comprising a synthetic resin based, as its main constituent, on methacrylate homopolymer or a methacrylate copolymer.

Example

It has been demonstrated that by controlling the solidification rate during strip casting and thus producing average primary particles essentially below $1 \mu\text{m}^2$ ¹ and finer distribution of especially iron rich particles, the potential harmful cathodic effect of such particles is substantially reduced.

The Al-alloy AA 3003 has been strip cast according to the method of the present invention at a cooling rate in a range from 10^2 to 10^3 °C/sec to Al-sheets at 4.5 mm thick and then cold rolled to 60 μm with optional inter-annealing during cold rolling. The 4.5 mm thick strip was cold rolled to 0.58 mm followed by an intermediate annealing. The annealing was undertaken in an air furnace by heating from room temperature to 340°C at 30°C/hour and soaking at 340°C for 3 hours. After cooling from 340°C to 200°C at 50°C/hour, the material was cooled in air. After annealing, the material was further cold rolled to 60 μm .

An identical alloy was applied to provide reference sheets produced by DC casting of the rolling ingot followed by hot rolling and cold rolling of the ingot to the identical gauge with typical commercial inter-annealing processes during cold rolling.

30

¹ The particle size is measured by SEM backscatter image analysis which is a two dimensional method. The particles are however found to be equiaxed meaning that a particle with an area of $1 \mu\text{m}^2$ has a corresponding volume of $1 \mu\text{m}^3$, i.e.: $\text{Volume}=(\sqrt{\text{Area}})^3$.

Fig. 1 shows the particle size and distribution of the fin materials before brazing.

Fig. 2 shows the particle size distribution of the fin material after brazing. The chemical composition of the alloys is given in Table 1. The number density of particles in the materials before and after brazing is listed in Table 2.

Alloy	Si	Fe	Cu	Mn	Mg	Zn	Ti
Strip cast 3003	0.1122	0.4055	0.0651	1.0560	0.00382	0.0103	0.0103
Hot rolled 3003	0.1	0.4	0.07	1.1		0.02	

Table 1

10

Alloy	Condition	Particle number	Area measured (μm^2)	Number density ($\times 10^4/\text{mm}^2$)
Fin stock from strip cast AA 3003	Pre-braze	637	5761.15	11.06
	Post-braze	986	5761.15	17.11
Fin stock from hot rolled AA 3003	Pre-braze	353	5761.15	6.13
	Post-braze	256	5761.15	4.44

Table 2

15

Fig. 3 is the scanning electron microscopic back scattering image of the particles in the strip cast fin material after brazing.

Fig. 4 is the scanning electron microscopic back scattering image of the particles in the hot rolled fin material after brazing.

20

Fig. 5 is the simulated brazing cycle utilised for the testing materials.

It is well known that the pitting corrosion in 3xxx series alloys is prone to initiate from coarse Fe-bearing particles. When increasing the size of the Fe-bearing particles the cathodic area will be increased in the alloy. As a consequence, the rate of pitting corrosion will be increased in the vicinity of the Fe-bearing particles.

5 This is detrimental to the corrosion performance of the alloy.

In general, as seen in Figs. 3 and 4, there are two types of Fe-bearing particles in AA 3003 alloys. One is $Al_6(Fe,Mn)$ exhibiting coarser particles and another one is $\alpha-AlMnFeSi$ (fine particles). From the results in the attachment, it can be seen that
10 the strip cast fin material contains dense fine particles of two types before and after brazing, and very few particles are larger than $1\mu m^2$. However, the particles in the hot rolled fin material have bimodal character consisting of small dispersoids of $\alpha-AlMnFeSi$ and coarse particles of $Al_6(Fe,Mn)$ (typical size larger than $5\mu m^2$) before and after brazing. After brazing, the number density of the particles in the
15 strip cast material is about four times as that in the hot rolled material (see Table 1). So, the size and distribution of the Fe-bearing particles in the fin alloy can be controlled and modified through continuous strip casting followed by proper processing. This is very beneficial for fin alloys in terms of corrosion performance.

20 Furthermore, as it has been mentioned previously that by provision of a flux retaining coating on such provided cast sheet surface, especially if the flux is (reactive) fluoride-based flux, it is possible to utilize the improved corrosion resistance of strip cast sheets in manufacturing of heat exchanger components. One example is that the continuous strip cast sheet can be used as tube to
25 combine with clad fin material in a heat exchanger; in this case, at least one of the flat surfaces of the said continuous cast sheet is coated with a reactive flux or a normal flux. Another example is that the continuous strip cast sheet can be used as header in a heat exchanger; in this case, at least one of the flat surfaces of the said continuous cast sheet is coated with Al-Si powders.

Claims

1. A method of producing aluminium alloy sheet material,
5 **characterised in** the following steps;
- continuous strip casting of a sheet at a predetermined solidification rate ensuring material microstructure exhibiting primary particles having average size below 1 micrometer², and
 - (cold) rolling of the strip cast sheet to an appropriate gauge with optionally
10 intermediate annealing during the cold rolling.
2. Method according to claim 1,
characterised in that
the sheets are further annealed during cold rolling.
15
3. Method according to claims 1 and 2,
characterised in that
the alloy is cast to 4.5 mm thick strip and cold rolled to 0.58 mm followed
by an intermediate annealing.
20
4. Method according to claims 1-3,
characterised in that
the intermediate annealing was undertaken in an air furnace by heating
from room temperature to 340°C at 30°C/hour and soaking at 340°C for 3
25 hours.
5. Method according to claims 1-4,
characterised in that
after cooling from 340°C to 200°C at 50°C/hour, the material was cooled
30 in air.

6. Method according to claims 2-5,
characterised in that
after annealing, the material was further cold rolled to 60 µm.
- 5 7. An aluminium alloy sheet,
characterised in that
its material microstructure exhibits primary particles having average size below 1 micrometer².
- 10 8. Aluminium alloy sheet according to claim 7,
characterised in that
the primary particles are iron-enriched particles ensuring improved pitting corrosion resistance.
- 15 9. Aluminium alloy sheet according to claim 7-8,
characterised in that
at least one of the flat surfaces is coated with a reactive flux retaining coating capable of providing joints in a brazing process, where the flat surface at least partially is coated with a flux retaining composition comprising a synthetic resin based, as its main constituent, on methacrylate homopolymer or a methacrylate copolymer.
- 20
10. Aluminium alloy sheet according to claims 7-9,
characterised in that
at least one of the flat surfaces is coated with a reactive flux or a normal flux to enable the sheet to be utilised as tube for clad fin in a heat exchanger.
- 25
11. Aluminium alloy sheet according to claims 7-9,
characterised in that
at least one of the flat surfaces is coated with Al-Si powders to enable the sheet to be utilised as header in a heat exchanger.
- 30

1/4

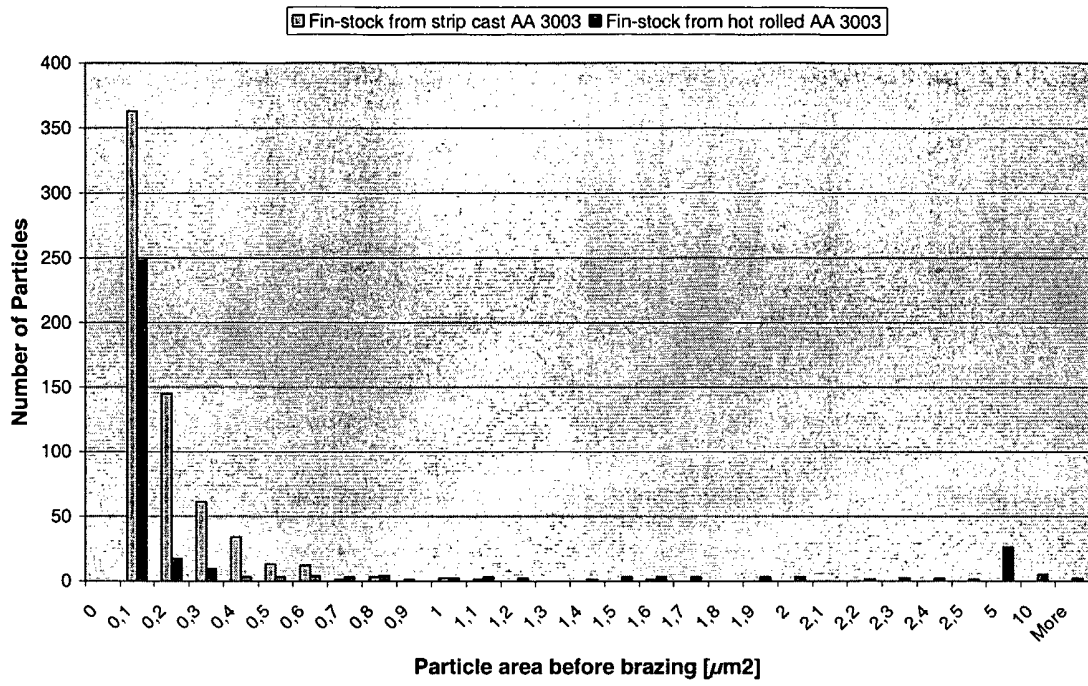


Fig. 1

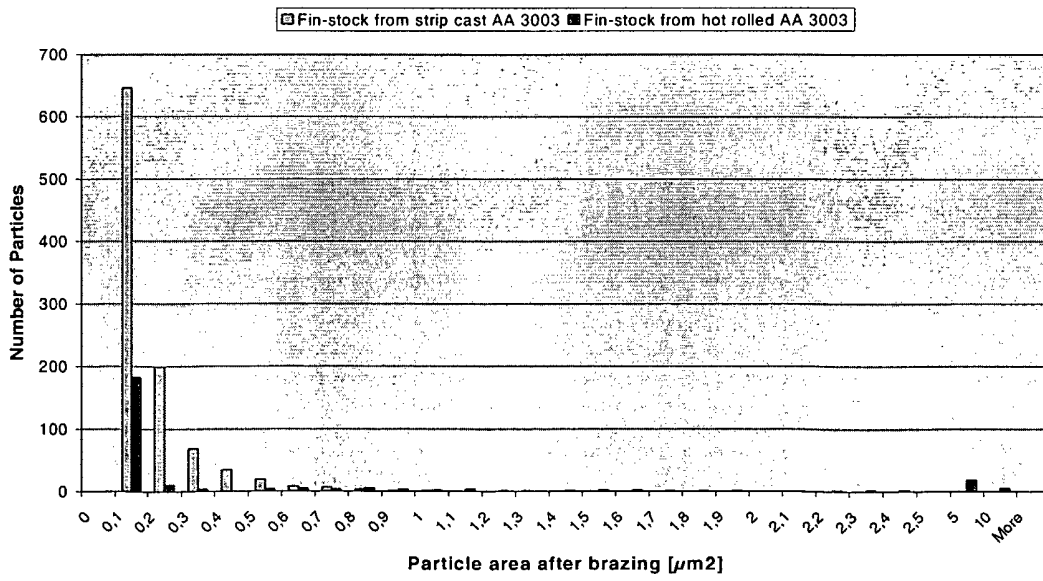


Fig. 2

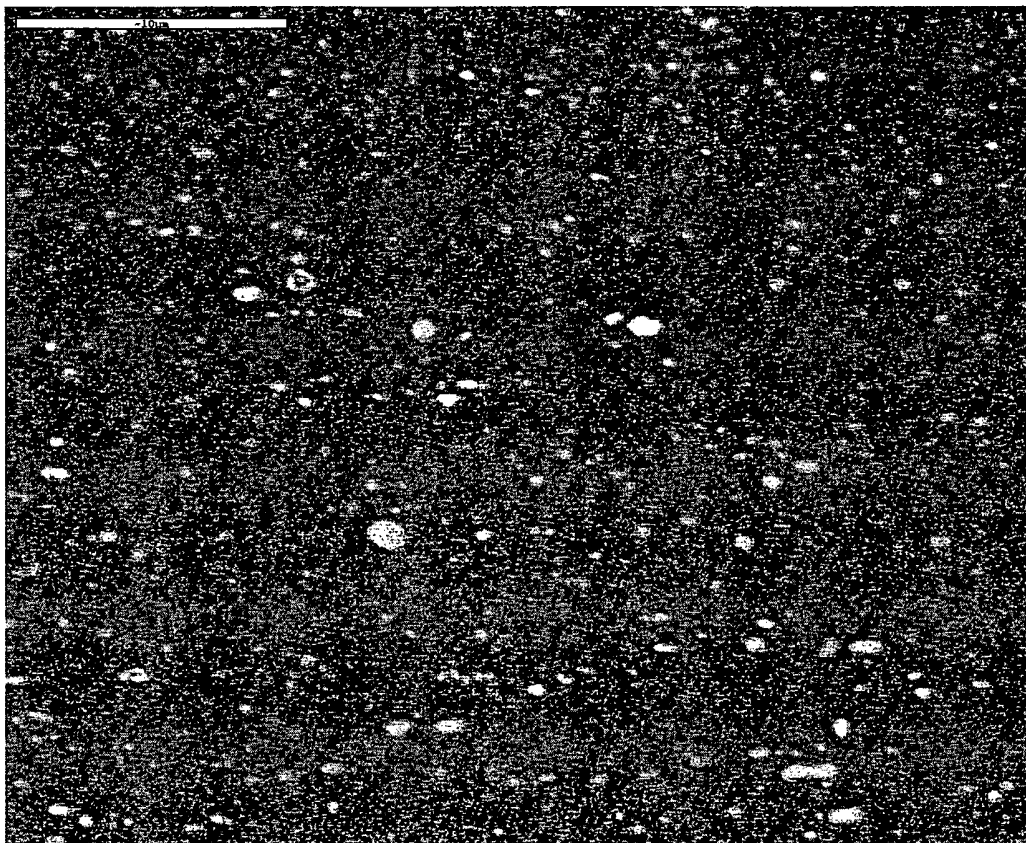


Fig. 3

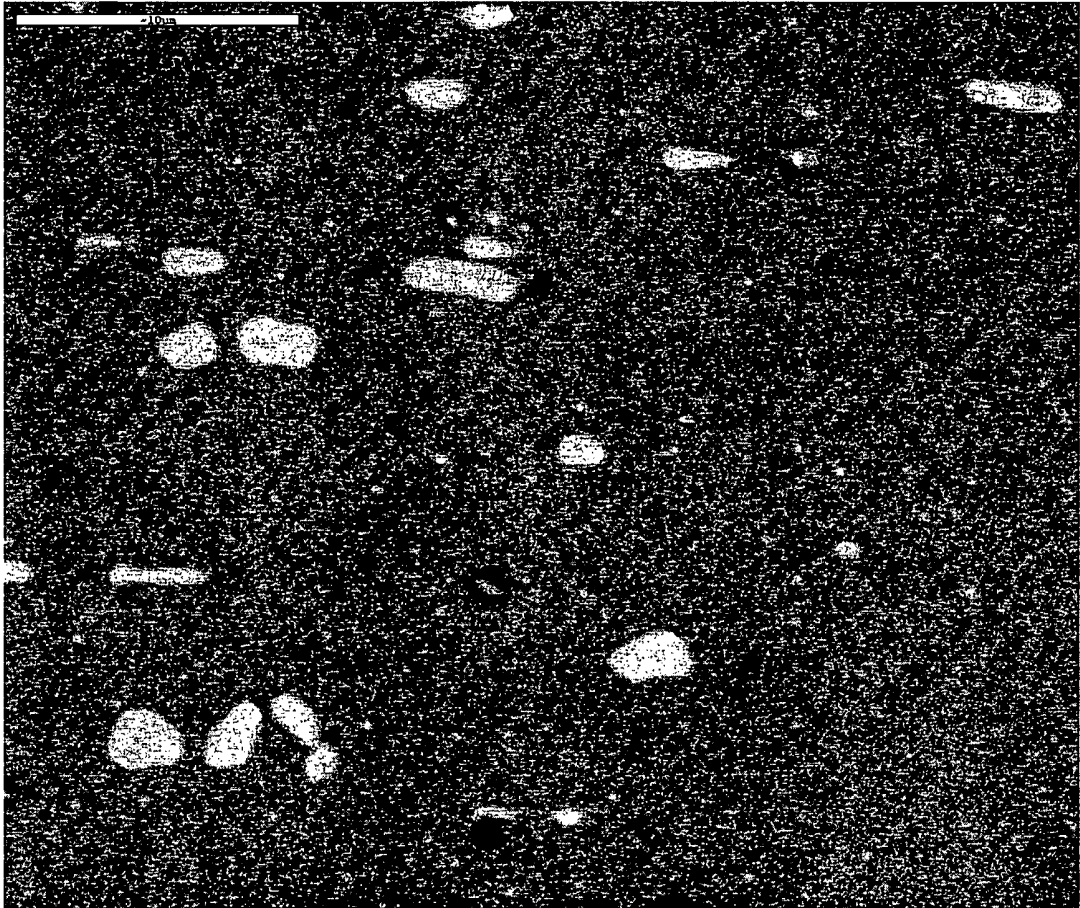


Fig. 4

4/4

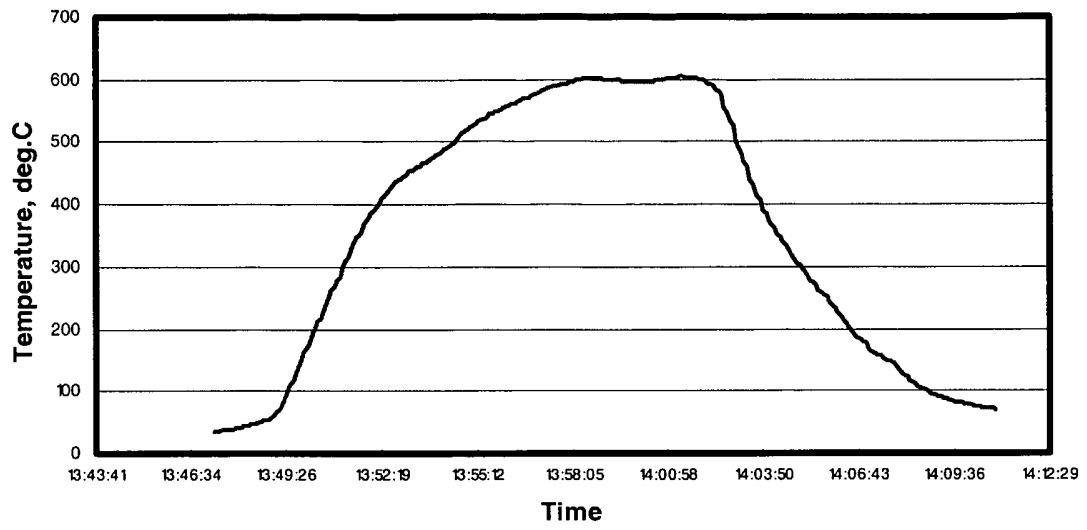


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 2004/000074

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C22C 21/00, C22F 1/04

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)

IPC7: C22C, C22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3827917 A (P.P. ZEIGLER ET AL), 6 August 1974 (06.08.1974), column 2, line 13 - column 3, line 45	1-6,7,8
A	--	9-11
X	US 6344096 B1 (STEPHEN F. BAUMANN ET AL), 5 February 2002 (05.02.2002), column 1, line 36 - line 56; column 3, line 25 - line 51	1-6,7,8
A	--	9-11

 Further documents are listed in the continuation of Box C.
 See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search 8 July 2004	Date of mailing of the international search report 13 -07- 2004
---	---

Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Nils Engnell/MP Telephone No. +46 8 782 25 00
--	---

INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 2004/000074

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4334935 A (LARRY R. MORRIS), 15 June 1982 (15.06.1982), column 1, line 1 - column 2, line 45	1-6,7,8
A	--	9-11
A	GB 1457697 A (SOUTHWIRE COMPANY), 8 December 1976 (08.12.1976), page 1, line 72 - page 2, line 41; page 4, line 18 - line 45	1-6,7-11
A	US 4021271 A (SIDNEY G. ROBERTS), 3 May 1977 (03.05.1977), column 1, line 44 - column 2, line 59	1-6,7-11
A	US 3852122 A (AKSEL OLA AARFLOT ET AL), 3 December 1974 (03.12.1974), column 2, line 19 - line 63	1-6,7-11

INTERNATIONAL SEARCH REPORT
Information on patent family members

30/04/2004

International application No.

PCT/NO 2004/000074

US	3827917	A	06/08/1974	DE	2029584	A	23/12/1970
				GB	1286720	A	23/08/1972
				JP	48037492	B	12/11/1973

US	6344096	B1	05/02/2002	NONE			

US	4334935	A	15/06/1982	AU	541329	B	03/01/1985
				AU	6976181	A	05/11/1981
				BR	8102605	A	19/01/1982
				CA	1137391	A	14/12/1982
				DE	3168588	D	00/00/0000
				EP	0039211	A,B	04/11/1981
				ES	501678	A	01/04/1982
				ES	8203975	A	16/07/1982
				GB	2075059	A,B	11/11/1981
				JP	1512058	C	09/08/1989
				JP	56169758	A	26/12/1981
				JP	63057492	B	11/11/1988
				MX	154956	A	14/01/1988
				ZA	8102645	A	28/04/1982

GB	1457697	A	08/12/1976	IT	1046736	B	31/07/1980
				ZA	7401430	A	26/02/1975

US	4021271	A	03/05/1977	NONE			

US	3852122	A	03/12/1974	AT	210273	A	15/04/1975
				AT	327573	B	10/02/1976
				AU	474737	B	29/07/1976
				AU	5298773	A	12/09/1974
				BR	7301720	D	00/00/0000
				CA	992358	A	06/07/1976
				CH	598355	A	28/04/1978
				DE	2311509	A	13/09/1973
				ES	412459	A	01/01/1976
				FR	2175850	A,B	26/10/1973
				GB	1419691	A	31/12/1975
				IN	138730	A	20/03/1976
				IT	980423	B	30/09/1974
				JP	49001418	A	08/01/1974
				NL	7303409	A	12/09/1973
				NO	131035	B,C	16/12/1974
				RO	62272	A	15/08/1977
				SE	396774	B,C	03/10/1977
