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(54) **High strength aluminium fin material for brazing**

(57) The invention refers to an aluminium alloy, a clad or unclad material for brazed products containing said alloy as a core, as well as a method of producing materials to be used in brazed products from said alloy. The material is suitable for controlled atmosphere brazing (CAB) using fluxes that manage higher Mg levels in the materials. The alloy is intended as a fin-stock material for brazed products, such as heat exchangers.

The alloy comprises 0.5 - 1.0 wt-% silicon, 0.25 - 0.6 wt-% magnesium, 0.3 - 0.7 wt-% manganese, and

0.05 - 0.25 wt-% zirconium, and optionally up to 4 % Zn, the balance consisting of aluminium and unavoidable impurities.

The method for producing the material comprises the steps of subjecting said alloy to a casting process and subjecting the cast alloy to hot rolling and a cold rolling process, possibly followed by an annealing process.

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Description

[0001] The present invention is related to an aluminium alloy intended as a fin-stock material for brazed products, such as heat exchangers, either as a braze clad material containing said alloy as a core or unclad. The alloy is heat treatable (precipitation hardenable) The material obtained has got a high strength after brazing, especially after an artificial ageing treatment, and gives a high corrosion resistance to the brazed product as it is sacrificial to the tube. The material may be used to make products by any brazing method, in particular the controlled atmosphere brazing method (CAB) when a flux that allows alloys with Mg is used.

[0002] To attain an aluminium alloy with a very high strength precipitation hardenable alloys must be used as the precipitation hardening mechanism gives the highest strength of the aluminium alloys. In present commercial brazing applications only the AlMgSi system can be used as the alloys using the other precipitation hardenable systems have a too low melting point compared to the melting interval of the standard braze filler alloys.

[0003] When aluminium components are heated in air, the surface layer oxidises and forms aluminium oxide. Even in the protective atmosphere in the CAB process some oxygen and water vapour are present, which will oxidise the surface. A flux is therefore provided to disrupt the aluminium oxide, and protect the surface during the brazing. When alloys containing Mg is brazed magnesium oxides are formed, which will not be broken down by the common fluxes. Magnesium fluoride compounds are found as residues, indicating a consumption of the flux by Mg.

[0004] Present manufacturers using CAB has therefore been limited to use alloys without Mg as fins, and common fin alloys are modified AA3003 variants with 1 to 3 wt-% Zn. The Zn is added to provide a sacrificial action of the fin, thereby protecting the tube from corrosion attacks. Another well-used alloy is the FA6815 from SAPA Heat Transfer [protected by patent SE-510272]. However with the advent of fluxes (WO-8604007, EP-0091231) that tolerate and allow higher Mg levels, alloys containing Mg may be brazed in CAB furnaces.

[0005] In combination with Si, Mg may form small precipitates that increase the strength of the alloy considerably. This mechanism is called age hardening. The AA6xxx series of alloys are based on the Mg and Si precipitates, but alloys in that series are generally not suitable for brazing, as most of them has a too high Mg content. Others are without Mn, reducing the sag resistance of the alloy. Age hardening alloys have not yet been utilised in a fin stock material to be brazed in the CAB process.

[0006] A challenge today is to manufacture light-weight components for the automotive market. A lot of research is therefore directed to reduce the weight of heat exchangers by using thinner strip. The new invention shows a higher strength compared to the presently used alloys, while the corrosion protection of the tubes is retained. This will allow thinner fins with retained strength of the brazed product, thereby reducing the weight compared to products brazed today. Alternatively, the higher strength can be utilised to give a more rigid brazed product that will withstand higher stresses, such as vibrations or pulsation of the internal pressure.

[0007] In AlMgSi alloys small Mg_2Si precipitates form during ageing, causing the strength to increase. Thus the trivial solution to increase the strength would be to increase the Mg and the Si contents, allowing more Mg_2Si to form. However, Mg reacts with the flux during brazing and this limits the amount of Mg. This is also true for the new fluxes that is said to tolerate Mg, but at a much higher level (levels of 0.66 wt.-% Mg has been reported in the literature [Garcia J, Mas-soulier C, Faille Ph, VTMS 5, Nashville, TN, May 14-17, 2001]).

[0008] US-6120848 discloses a method for providing the flux onto the surface of a brazing sheet, by mechanically embedding the flux in the cladding. It is mentioned that CsF fluxes allows a higher Mg in the core materials.

[0009] In US-5771962 a modified flux, containing caesium and/or lithium fluoride, and a modified braze cladding is used to braze the standard 1000, 3000, 5000 or 6000 alloys containing up to 3 wt-% Mg by CAB (Controlled Atmosphere Brazing). The braze cladding on the tube surfaces contains, apart from the main alloying element silicon, lithium, magnesium, sodium, and optionally caesium.

[0010] In US-6234243 an attempt is made to increase the strength of aluminium heat exchangers tube material by adding Mg, and protecting the braze cladding with an intermediate Al-Li alloy layer. To improve the brazeability Cs is added to the braze cladding alloy, and finally a modified flux with Cs and Li is recommended. This is an expensive way to achieve high strength.

[0011] The effort put into trying to find a way to increase the strength of fin materials above that achievable with the standard aluminium alloys shows, exemplified by the above patent documents, shows that there has been a long felt need for a stronger alloy that may be brazed using CAB. One example can be found in the patent WO 01/36697 (Corus), where a fin material with the following composition (in wt.-%) is disclosed: 0.7 - 1.2 Si (0.75 - 1.0 preferred), up to 0.8 Fe (0.2 - 0.45 preferred), up to 0.5 Cu (0.2 - 0.4 preferred), 0.7 - 1.2 Mn (0.8 - 1.0 preferred), up to 0.35 Mg (0.2 - 0.35 preferred), up to 3 Zn, up to 0.25 Zr (0.05 - 0.15 preferred), up to 0.2 In (0.01 - 0.1 preferred), up to 1.5 Ni (0.3 - 1.2 preferred), up to 0.2 Ti, and up to 0.25 of Cr and V. It is stated in the patent that a key feature is the, compared to the standard AA3xxx alloys, relatively high Si content in combination with a medium Mn content, increasing the strength. The alloy is not reported to be age hardenable, and the amount of Mn will certainly make the material quench sensitive, i.e. the age hardening response, if any, will be low.

[0012] None of the above documents discloses a high strength, heat treatable aluminium alloy suitable as fin-stock for CAB according to this invention.

Summary of the invention

[0013] The object of the present invention is to provide a high strength, heat treatable, aluminium alloy while keeping the Mg content sufficiently low for brazing in a CAB furnace using a flux that tolerates Mg. Another object is to provide a material with a sufficient corrosion sacrificial action to protect another material brazed to the invention. Preferred applications are fins for heat exchangers, like automotive radiators, heaters, or charge-air coolers. Other applications are not excluded.

[0014] An important aspect considering the strength of heat treatable brazing alloys is the quench sensitivity. A quench sensitive alloy must be cooled rapidly after the solutionising treatment (i.e. the brazing operation) in order to keep the Mg and Si atoms in solid solution. A high Mn content will increase the quench sensitivity.

[0015] The invention will now be described in more detail, references below being made to the accompanying drawings wherein

Figure 1 shows the yield (Rp0.2) and the tensile strength (Rm) of the invented alloy compared to two reference materials after a braze simulation with cooling rates of 0.7°C/s and 2.5°C/s, natural ageing at room temperature.

Figure 2 shows the tensile strength (Rm) of the invented alloy after a braze simulation with a cooling rate of 0.7°C/s and 2.5°C/s, artificial ageing at different temperatures.

Figure 3 shows the yield strength (Rp0.2) of the invented alloy after a braze simulation with a cooling rate of 0.7°C/s and 2.5°C/s, artificial ageing at different temperatures.

Figure 4 shows the sagging test jig.

[0016] Note that standard materials available presently are not age hardenable after a controlled atmosphere brazing cycle. The tensile strength of the standard material AA3003 is about 110 MPa and that of the state of the art FA6815 is about 135 MPa. The yield strength of the standard material AA3003 is about 40 MPa and that of the state of the art FA6815 is about 50 MPa. The alloy of the invention has a notably higher strength than the presently available alloys.

[0017] The reason for the limitation of the composition of the alloy according to the present invention and its range will now be described.

[0018] The concentration of silicon should be 0.5 - 1.0 wt-%, preferably 0.6 - 0.9 wt-%. Below 0.5 wt-% the ageing response is low, above 1.0 wt-% the solidus temperature of the alloy is significantly lowered.

[0019] Magnesium increases the strength by forming Mg₂Si precipitates during ageing, but lowers the brazeability by reacting with the flux, even when the flux contains Cs or Li. The Mg content could therefore be as low as 0.25 wt-% and as high as 0.6 wt-%. Below the lower limit the alloy would not give a sufficient number of the Mg₂Si precipitates, and a high strength would not be obtained. The more Mg the higher the strength, but with a too high level the brazeability will be reduced, and furthermore there is a risk for incipient melting of the material at the brazing temperature. However, the preferred Mg level will depend on both the used flux and the used tube material. Different flux mixtures are available which have different tolerances to Mg [Garcia et al., cited previously]. Thus, if a flux with a high Mg tolerance and a tube material without Mg is used, then an alloy with 0.5 - 0.6 wt-% could be used, while another flux with less tolerance and/or a tube material with some Mg would limit the Mg in the fin.

[0020] Optionally Zn is added, up to 4 %. Zn will increase the sacrificial action of the fin material and the level must be optimised together with the tube material.

[0021] To improve the sagging resistance 0.1 - 0.3 wt-% zirconium, preferably 0.05 - 0.25 wt-% is added to the alloy. Zr is distributed as small Al₃Zr in the material. They will inhibit the recrystallisation, giving large grains of the material after brazing. Below 0.05 wt-% this effect is negligible, above 0.3 wt-% coarse precipitates are formed which will reduce the effect and the workability of the material.

[0022] Manganese in solid solution increases the strength, however the quench sensitivity is also increased. Thus, a low Mn content is beneficial to the strength if cooling rates are low. Furthermore, Mn is beneficial to the sagging resistance and corrosion resistance. The Mn content should be 0.3 - 0.7 wt-%, preferably 0.4 - 0.7 wt-%, most preferably 0.5 - 0.7 wt-%.

[0023] Fe has an adverse effect on the corrosion resistance and in higher amounts on the sagging resistance. It is therefore limited to 0.3 wt-%.

[0024] Copper is avoided in the alloy. Even though copper will further increase the strength, it has a negative influence on the corrosion behaviour. The electrochemical potential will increase, thereby reducing the anodic action and the protection of the tubes by the fin material.

[0025] Nickel is also avoided in the alloy. Nickel increases the risk for obtaining small grains in the product, and thereby reduce the sagging resistance.

[0026] The claimed material is produced by casting an aluminium alloy according to the invention, and thereafter subjecting the obtained material to a hot rolling and a cold rolling process. After said casting process the material may be scalped and clad with at least one additional layer. The material may be interannealed between two cold rolling passes, and partially or fully annealed after the final cold rolling step. The annealing step may also be omitted.

Example 1

[0027] An alloy was designed according to the composition described above. The actual composition is shown in Table 1, together with the limits for two reference materials. The material was first scalped, hot rolled, and then cold rolled down to 0.1 mm, with an interannealing. Samples for tests were extracted at 0.5 mm (not interannealed) and in the final gauge.

The 0.5 mm material was braze simulated with two different heating cycles, basically giving cooling rates of 2.5°C/s and 0.7°C/s between 400 and 200°C. This represents both an optimal cooling rate and one usually surpassed by brazing furnaces in practice.

The increase in strength with time at room temperature is shown in Figure 1. It is compared with the strength of the standard material AA3003 and the high strength fin material FA6815, the present state of the art. The increase in strength after natural ageing is substantial for the new material, even though the cooling rate after brazing is not optimal.

Designation	Si	Fe	Cu	Mn	Mg	Zn	Zr
New invention	0.88	0.27	0.02	0.69	0.26	0.7	0.12
Reference AA3003 +Zn	<0.6	<0.7	0.05 - 0.20	1.0 - 1.5	<0.05	*	<0.05
Reference FA6815	0.5 - 1.0	<0.7	<0.10	1.4 - 1.8	<0.05	1.2 - 1.8	0.05 - 0.20
Reference AA6063	0.20 - 0.6	<0.35	<0.10	<0.10	0.45 - 0.9	<0.10	<0.05

* The Zn in fin materials may vary, depending on the desired anodic protection of the tube. Common levels of Zn in fins are between 1 and 2.5 wt.-%. Zn has only marginal effects on other properties like strength and sagging.

Example 2

[0028] Material from the same braze simulations as in Example 1 was artificially aged at different temperatures after a delay of one day. Three temperatures were used: 160, 180, and 195°C. The tensile strength of the samples is shown in Figure 2 and the yield strength in figure 3. As can be seen, tensile strengths of 250 MPa and yield strengths surpassing 200 MPa may be obtained.

The material show a substantial age hardening response, and yield strengths more than three times as high as that of the standard materials in brazing of today were achieved.

Example 3

[0029] The sagging resistance of the material was measured by mounting thin strip samples (gauge 0.1 mm) in a special jig, allowing 60 mm lever length (Figure 4). The material in the jig was then subjected to a braze cycle with a 10 minute dwell at 600°C. The deflection is measured when the material has cooled off.

The mean deflection for the new invention was 27.6 mm, which may be compared to 17 to 23 mm for FA6815 and 35 to 40 mm for the standard heat treatable material AA6063. The new invention shows a reasonable sagging resistance.

Claims

1. An aluminium alloy for brazed products with high strength, **characterized in that** the alloy comprises 0.5 - 1.0 wt-% silicon, 0.25 - 0.6 wt-% magnesium, 0.3 - 0.7 wt-% manganese, and 0.05 - 0.25 wt-% zirconium, and optionally up to 4 % Zn, the balance consisting of aluminium and unavoidable impurities, the Fe in said impurities being controlled up to 0.3%.
2. An aluminium alloy according to claim 1, **characterized in that** the manganese content is 0.4 - 0.7 wt-%.

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3. An aluminium alloy according to claim 1, **characterized in that** the manganese content is 0.5 - 0.7 wt-%.
4. An aluminium alloy according to any of claims 1-3, **characterized in that** the silicon content is 0.6 - 0.9 wt-%.
- 5 5. A clad material for brazed products with high strength, **characterized in that** the core alloy comprises 0.5 - 1.0 wt-% silicon, 0.25 - 0.6 wt-% magnesium, 0.3 - 0.7 wt-% manganese, and 0.05 - 0.25 wt-% zirconium and optionally up to 4 % Zn, the balance consisting of aluminium and unavoidable impurities, the Fe in said impurities being controlled up to 0.3%.
- 10 6. A clad material according to claim 5, **characterized in that** the manganese content is 0.4 - 0.7 wt-%.
7. A clad material according to claim 5 or 6, **characterized in that** the manganese content is 0.5 - 0.7 wt-%.
- 15 8. A clad material according to any of claims 5-7, **characterized in that** the silicon content is 0.6 - 0.9 wt-%.
9. A method of producing a material from the alloy of any of claims 1-8, **characterized by** the steps of
- subjecting said alloy to a casting process,
 - subjecting the obtained material to a hot rolling process
 - 20 - subjecting the obtained material to a cold rolling process.
10. The method as claimed in claim 9, **characterized in that** after said casting process the material is scalped and clad with at least one additional layer.
- 25 11. The method as claimed in claims 9 or 10, **characterized in that** after said cold rolling the material is subjected to an annealing process.
12. Use of the material in any of claims 1-8 to produce a fin-stock for heat exchangers.
- 30 13. Use of the material in any of claims 1-8 in a brazing process where an inert atmosphere is used.
14. Use of the material in any of claims 1-8 in a brazing process using a controlled atmosphere and a suitable flux.

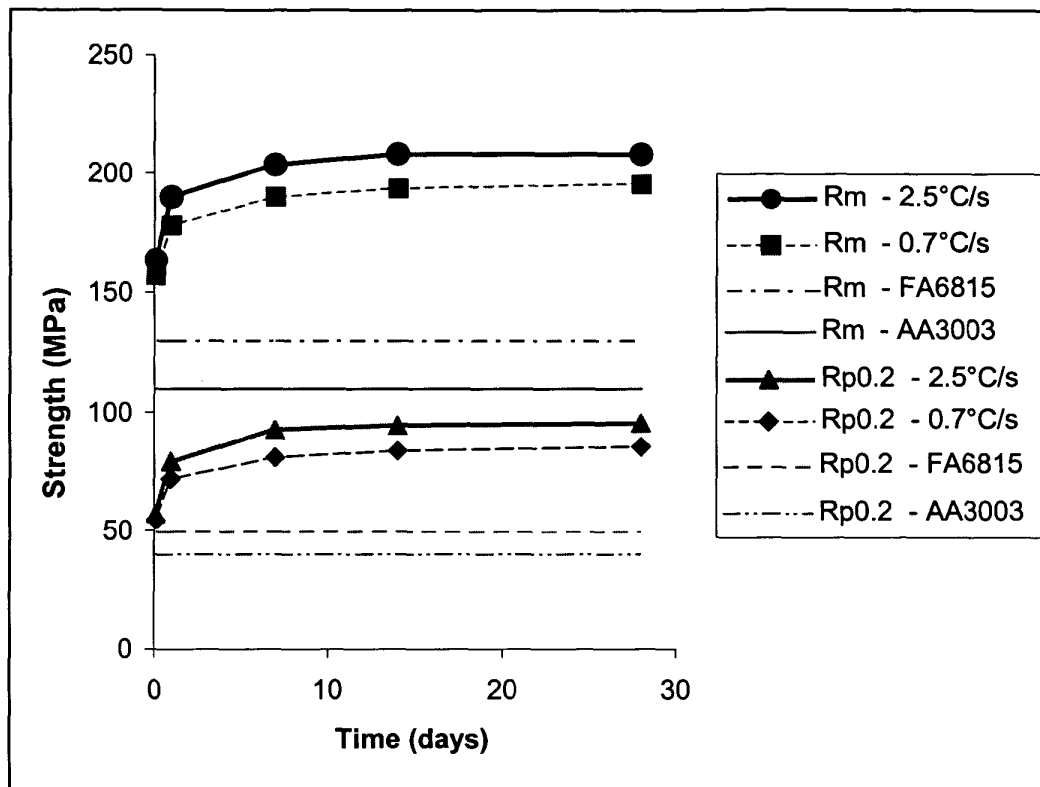


Figure 1.

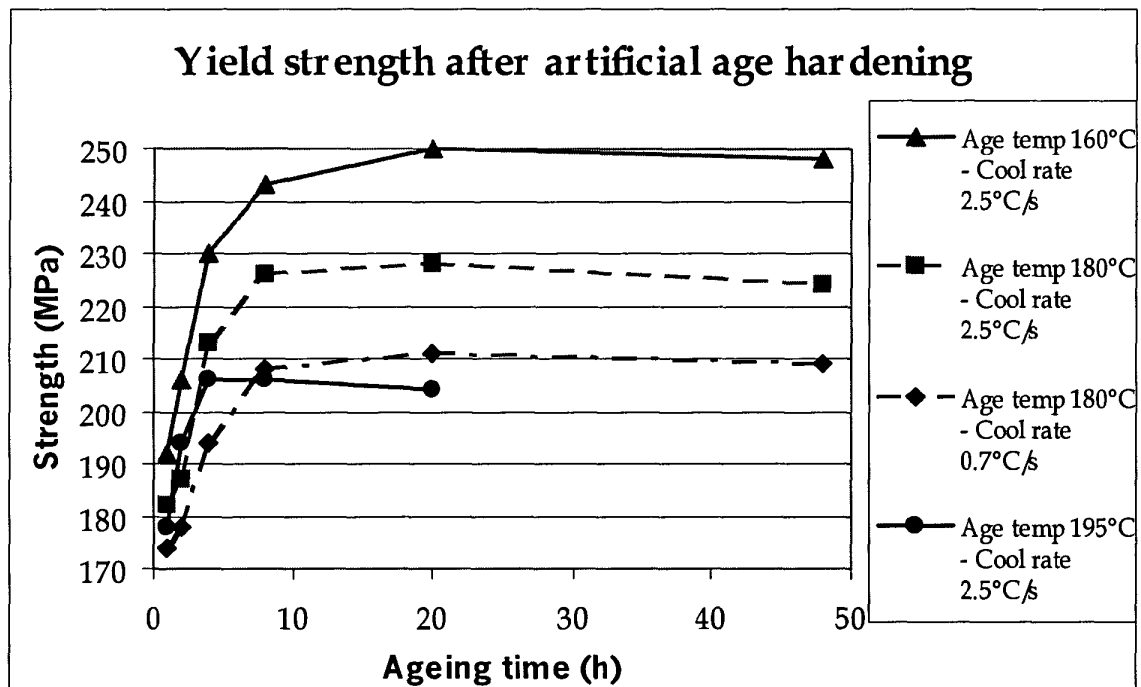


Figure 2

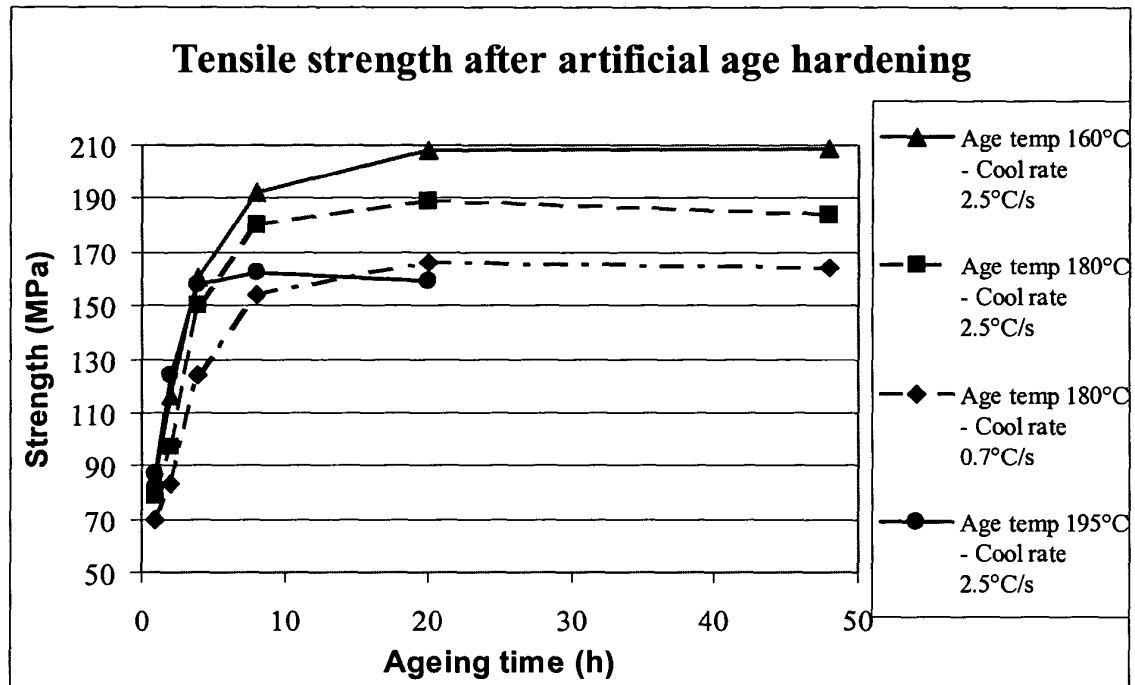


Figure 3

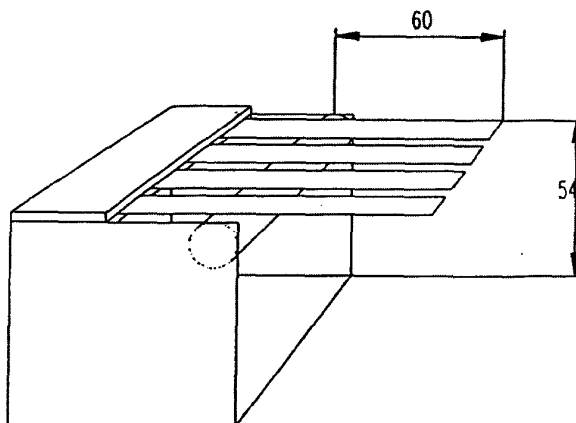


Figure 4



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EUROPEAN SEARCH REPORT

Application Number
EP 03 07 8132

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			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C22C C22F B32B B23K F28F
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 9 March 2004	Examiner González-Junquera, J
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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