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### (54) **Method for the manufacture of aluminium alloy sheet**

(57) A method for the manufacture of a sheet of an A1MgSi alloy of the AA6xxx type containing Si in an amount of 0.4 to 1.7 wt% and Mg in an amount of 0.2 to 0.9 wt%, comprises the following steps carried out in the following sequence:-

- (i) cold-rolling of the alloy to the final desired sheet thickness,
- (ii) solution heat treatment of the sheet,
- (iii) cooling from the solution heat treatment temperature to below 150°C at a cooling rate of at least 100°C/min. and further cooling to below 50°C,

- (iv) holding the sheet below 50°C for a holding time of not more than 30 minutes after the end of step (iii),
- (v) immediately after step (iv), heating the sheet to a predetermined holding temperature within the temperature range 165-185°C,
- (vi) maintaining the sheet at the predetermined holding temperature for a holding time in the range 60 to 600s, before cooling again.

Steps (iv) to (vi) particularly effect a preliminary ageing to prepare the sheet for a subsequent paint-bake as an automotive body part.

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**Description**

The invention relates to a method for the manufacture of a sheet of an AlMgSi alloy of the AA6xxx type. Such sheet is suitable for example for forming into automotive body parts.

Heat-treatable AlMgSi alloys of the AA6xxx type are being used increasingly for automotive body parts in which, besides good formability of the aluminium sheet, the strength after undergoing a painting cycle plays an important role. The requirements imposed on the aluminium sheet used for the automotive body parts include good formability, a low and stable yield point, a high surface quality including among other things that no stretcher strains are present following shaping or deforming into a bodywork panel.

Conventionally, such aluminium sheet is produced by cold-rolling to final thickness, followed by solution heat treatment and quenching from solution heat treatment temperature so as to cool to below 150°C at a cooling rate of at least 100°C/min. Following this cooling the aluminium sheet is then aged to obtain the desired level of properties. For use in the automotive industry the aluminium sheet, following shaping by for example pressing at room temperature, is provided with one or more paint layers. In this manner good corrosion resistance is obtained. Such a paint layer is fast-cured by maintaining it for some time at an elevated temperature, for example 20-40 min at approximately 190-200°C. Such a treatment is often designated by the terms 'paint-bake' or 'paint-baking'. Going through such a treatment is designated by the term 'paint-bake cycle'.

Artificially ageing the aluminium sheet and curing the paint layer usually largely coincide. The trend among automotive manufacturers is to reduce and lower the time and/or temperature respectively of the paint-bake, for example to 15-30 min at approximately 160-190°C. This trend is attributable to the use of different paints and the need for energy saving. A consequence of this is that among other things the aluminium sheet of the type indicated does not age or does not age adequately because of a natural incubation time for the ageing, or attains an unsatisfactory low level of mechanical properties.

It is known that adding copper as an alloying element to the aluminium sheet causes an accelerated reaction to ageing (ageing response) during paint-baking, so that the desired properties are still attained at an adequate level. A disadvantage of adding copper is that it will cause the corrosion resistance of the aluminium sheet fall to an unacceptable level.

Proposals have been made for a preliminary ageing treatment to improve the properties of the sheet following the paint-bake. Particularly, WO 96/07768 (Alcan) discloses a method for AlMgSi and AlMgSiCu alloys in which, after quenching from solution heat treatment and before any substantial age hardening has taken place, at least one subsequent heat treatment is performed by heating to a peak temperature in the range 100-300°C, preferably 130-270°C and holding this peak temperature for less than 1 minute, most preferably for 1 second or less. When one such heat treatment only is performed, the peak temperature selected is 190-300°C.

US-A-3 135 633 (Hornus) proposes an ageing process of wrought products of AlMgSi alloy in which, within 10 minutes of quenching from solution heat treatment, a preliminary ageing temperature of 100 to 250°C is reached and maintained for 1 to 10 minutes as part of a continuous process, and a final ageing is thereafter performed of for example 10 hours at 160°C. The example of preliminary ageing temperature is 140°C. The alloy composition is not specified.

An object of the present invention is to provide a method of manufacturing an aluminium sheet of the AA6xxx type which, after the paint-bake cycle according to the trend described above, has the desired properties, while the addition of copper is unnecessary. Another object of the invention is to provide a method by which the aluminium sheet may be manufactured on an existing production line without too many modifications. Yet another object of the invention is that the disadvantageous effect of the natural ageing on the mechanical properties after the paint-bake cycle can be reduced.

The method according to the invention is set out in claim 1. This method achieves the effect that during a paint-bake cycle for example according to the trend described above, the aluminium sheet artificially ages adequately to allow the desired properties to be obtained at an adequate level. In particular, because the sheet is heated to a predetermined holding temperature in the range of 165-185°C, there is achieved the effect that the ageing response during the paint-bake cycle is optimal for the sheet of the composition specified.

Preferably the holding time of the aluminium sheet in this holding temperature is between 60-300 s, and more preferably is between 60-180 s. If the holding time is too long, then so-called over-ageing will occur. This makes the strength increase to an inadmissible level while the ductility decreases. If the holding time is too short, then during the paint-bake cycle there will still be an incubation time, and inadequate ageing will be likely to occur during that cycle.

Preferably in step (iv) the aluminium sheet is held at a temperature below 50°C for a time period preferably of no more than 15 min before being heated directly to the holding temperature of steps (v) and (vi). In a continuous process, this time period may be only a few seconds. The aluminium sheets of the type of this invention are sensitive to natural ageing. If the holding time during step (iv) is too long, then large Mg-Si clusters can form which essentially are responsible for the incubation time during the paint-bake cycle.

An advantage of the heat treatment in accordance with the invention directly following the quenching from heat

treatment for improving the ageing response of the aluminium sheet during the paint-bake cycle is that it is simple to apply in existing continuous production lines for the aluminium sheet because the holding time at the holding temperature in the range 165-185°C is relatively short. It is alternatively possible to carry out the method in accordance with the invention batchwise.

5 Preferably, in the manufacture of an automotive part, the heat treatment of steps (v) and (vi) in the invention is the sole heat treatment between the solution heat treatment and the paint-bake following shaping of the sheet into the desired shape. Thus after this single heat treatment, the sheet is cooled to room temperature and is ready for storage, transport and shaping as appropriate. Considerable time may elapse before the sheet is shaped and subjected to paint-bake, without loss of the desired properties both in shaping and following the paint-bake.

10 The cold-rolling of the aluminium sheet to final thickness and the solution heat treatment of such sheet are well known in the art and need not be described here.

By a suitable choice of composition of the alloy the desired mechanical properties are obtained, and the aluminium sheet also forms well, has good corrosion resistance, good paintability, good weldability especially for spot welding and a good surface quality.

15 Preferably the aluminium sheet used in the invention has the composition in weight percent as follows: 0.4-1.7 Si, 0.2-0.9 Mg, 0.25 Mn (maximum), 0.2 Cu (maximum), 0.5 Fe (maximum), the balance essentially aluminium and unavoidable impurities.

Preferably the Si content is 0.8-1.5 wt%. This achieves the effect of improving the mechanical properties. More preferably the Si content is 1.0-1.3 wt%. This achieves the effect of optimizing the mechanical properties and formability for application of the aluminium sheet in automotive body parts.

20 The Mg content is preferably 0.2-0.6 wt%. Cooperation with the Si allows Mg-Si clusters or precipitates to form which contribute to the mechanical properties of the aluminium sheet. More preferably the Mg content is 0.25-0.45 wt% because an optimum formability is achieved when the Si/Mg ratio is approximately 3.

25 The Mn content is preferably 0.05-0.20 wt%. In the case of a relatively high Mn content, for example over 0.3%, the ductility reduces to an unacceptable level as the Mn content increases. If the Mn content is too low, for example lower than 0.05%, the Mn may not contribute sufficiently to an effective grain refinement during the solution heat treatment as a consequence of the formation of too few so-called dispersoids. The optimum combination for the desired contribution to the grain refinement effect following solution heat treatment and the decreasing elongation as the Mn content increases is obtained at 0.05-0.20 wt% Mn.

30 It is possible that dispersoid-forming alloying elements other than Mn can also be used for this purpose, such as for example Cr or Zr. If Cr or Zr is added at 0.05-0.25 wt%, then virtually identical results are achieved in respect of grain size following solution heat treatment as with Mn in that range. This is because the formed dispersoids are of the same order of size as when Mn is added, which is a consequence of the interaction of Zr or Cr with the Si and Mg. Adding Zr or Cr to an AA6xxx type alloy produces a significant improvement with respect to the grain size, but the costs for alloys containing Zr or Cr will be higher than if Mn is added in the same range. Moreover the value and usefulness of scrap material containing Zr or Cr is low. For this reason Zr or Cr is preferably not present to the aluminium sheet used in the invention other than any which is coincidentally or unavoidably present in the recycled scrap being used.

35 The Fe content has a great influence on the formability of the aluminium sheet. With a high Fe content, for example over 0.5 wt%, relatively large intermetallic compounds form which greatly reduce the formability. A low Fe content is therefore desirable. The Fe present also contributes to the control of the grain size in the sheet during solution heat treatment. The intermetallic compounds containing iron can favourably affect the nucleation process during solution heat treatment so that a small grain size occurs. Good results are achieved in the aluminium sheet in accordance with the invention with an Fe content not more than 0.3 wt%. More preferably the Fe content is 0.15-0.30 wt%. In this range the best compromise is obtained between a good formability and the favourable contribution to the grain size during solution heat treatment.

45 The alloying element Cu can make a considerable contribution to the increase in the mechanical properties of the aluminium sheet. It may be generally known that as Cu content in the aluminium sheet increases, the corrosion resistance greatly decreases. Bearing in mind the applications of the aluminium sheet in for example automotive body parts, good corrosion resistance is especially important. Therefore the Cu content in the aluminium sheet in this invention should generally be low. For an optimum corrosion resistance the Cu content must preferably be lower than 0.1 wt%. Cu therefore preferably is deliberately not added to the alloy and is not present other than that coincidentally or unavoidably present in recycled scrap being used.

50 The invention also consists in a sheet, e.g. one suitable for application in automotive body part manufacture, made in accordance with the invention. The invention further consists in such a sheet which is in shaped non-planar form and is optionally painted by a paint-bake process.

55 The invention will now be illustrated by non-limitative examples.

Example 1

Cold-rolled aluminium sheets of an AA6xxx alloy having the alloying elements (in wt%) 1.0% Si, 0.4% Mg, 0.26% Fe, 0.1% Cu and 0.05% Mn were conventionally solution heat treated and quenched in water. Then five different treatments (I-IV) were carried out. These treatments were:

- I 14 days natural ageing at room temperature;
- II 3 hours at 100°C following the solution heat treatment;
- III 1 day natural ageing followed by 4 hours at 115°C;
- IV holding for 1 minute at 200°C;
- V holding for 2 minutes at 175°C.

The heat treatments IV and V were both performed within 30 minutes of the quenching from solution heat treatment temperature, and were followed by cooling again to room temperature.

Then the uniform elongation (Ag), the total elongation (A80), and the work hardening exponent "n" of the aluminium sheets were determined. The results are shown in Fig. 1, for the five treatments I-V.

Following the heat treatment the aluminium sheets from the treatments I-V underwent various paint-bake cycles and then the 0.2% proof stress was determined. The results are shown in Fig. 2 which specifies the time [min] and temperature [°C] of the paint-bake cycles.

It can be seen from these results that the heat treatment V in the range in accordance with the invention contributes to a higher strength following subjection to a paint-bake cycle. It can also be seen that natural ageing prior to the heat treatment in accordance with the invention results in lower strength following subjection to the paint-bake cycle. It can further be seen that the duration and the temperature of the paint-bake cycle has a great influence on the final strength of the aluminium sheet. In particular good results are obtained with the heat treatment V in accordance with the invention in the case of the relatively short duration and low temperature of the paint-bake cycle. A holding time shorter than 1 min in a temperature range of 165-185°C is inadequate for obtaining sufficient strength following the paint-bake cycle. The short duration heat treatment of the invention is economical and is easily carried out in a continuous production line.

Example 2

Specimens suitable for mechanical testing in a laboratory were taken from cold-rolled coils and were solution heat treated at 570°C for 10 sec and then quenched in water. Then the specimens were naturally aged for 12 days and tested at room temperature. Aluminium sheets comprising the alloying elements as set out in Table 1 below were tested.

The influence of the concentration of alloying elements on the work hardening exponent "n" was determined and the results are given in Fig. 3. Among other things to be seen from this is that the Fe content has little effect on the "n" value of the alloys, while adding the elements Mn, Cr and Zr considerably reduces the "n" value, especially for the alloys containing Cr. For the alloys containing Mn with an Mn content of 0.1% or more, the "n" value attains a virtually constant level.

Also the effect of the concentration of alloying elements on the uniform elongation (Ag), and the total elongation (A80), was determined, the results being given in Fig. 4. From this it can be seen that for an increasing content of alloying elements the formability (ductility) reduces. Particularly the A80 value reduces with an increasing Fe content and the Ag value reduces in the case of alloys containing Mn and Cr. Adding Zr has little effect on the ductility of the alloys.

Table 1

Alloy composition of the tested aluminium sheets (wt%). Balance Al.						
Sheet	Si	Mg	Fe	Mn	Zr	Cr
1	1.11	0.34	0.15	-	-	-
2	1.13	0.37	0.26	-	-	-
3	1.17	0.37	0.30	-	-	-
4	1.19	0.36	0.25	-	0.06	-
5	1.08	0.36	0.25	-	0.10	-
6	1.25	0.36	0.27	-	0.15	-
7	1.18	0.35	0.22	0.10	-	-
8	1.18	0.37	0.27	0.15	-	-

Table 1 (continued)

Alloy composition of the tested aluminium sheets (wt%). Balance Al.						
Sheet	Si	Mg	Fe	Mn	Zr	Cr
9	1.09	0.34	0.20	-	-	0.10
10	1.19	0.35	0.20	-	-	0.15

The sheets containing 0% of the alloying elements Mn, Zr or Cr (in Figs. 3 and 4) are identical to sheet 2 of Table 1.

## Claims

1. Method for the manufacture of a sheet of an AlMgSi alloy of the AA6xxx type containing Si in an amount of 0.4 to 1.7 wt% and Mg in an amount of 0.2 to 0.9 wt%, comprising the following steps carried out in the following sequence:-

- (i) cold-rolling of the alloy to the final desired sheet thickness,
- (ii) solution heat treatment of the sheet,
- (iii) cooling from the solution heat treatment temperature to below 150°C at a cooling rate of at least 100°C/min. and further cooling to below 50°C,
- (iv) holding the sheet below 50°C for a holding time of not more than 30 minutes after the end of step (iii),
- (v) immediately after step (iv), heating the sheet to a predetermined holding temperature within the temperature range 165-185°C,
- (vi) maintaining the sheet at said predetermined holding temperature for a holding time in the range 60 to 600s, before cooling again.

2. Method according to claim 1 wherein in step (vi), the holding time is in the range 60 to 300s.

3. Method according to claim 2 wherein in step (vi) the holding time is in the range 60 to 180s.

4. Method according to any one of claims 1 to 3 wherein in step (iv) the holding time is less than 15 minutes.

5. Method according to any one of claims 1 to 4 wherein the composition of the alloy is, in wt%:-

Si	0.4 to 1.7
Mg	0.2 to 0.9
Mn	≤ 0.25
Cu	≤ 0.2
Fe	≤ 0.5

balance Al and unavoidable impurities.

6. Method according to any one of claims 1 to 5 wherein the amount of Si in the alloy is 0.8 to 1.5 wt%.

7. Method according to claim 6 wherein the amount of Si is 1.0 to 1.3 wt%.

8. Method according to any one of claims 1 to 7 wherein the amount of Mg in the alloy is 0.2 to 0.6 wt%.

9. Method according to claim 8 wherein the amount of Mg is 0.25 to 0.45 wt%.

10. Method according to any one of claims 1 to 9 wherein the amount of Mn in the alloy is 0.05 to 0.20 wt%.

11. Method according to any one of claims 1 to 10 wherein the amount of Fe in the alloy is not more than 0.3 wt%.

12. Method according to claim 11 wherein the amount of Fe is 0.15 to 0.3 wt%.

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13. Method according to any one of claims 1 to 12 wherein the amount of Cu in the alloy is not more than 0.1 wt%.

14. Aluminium alloy sheet made by the method of any one of claims 1 to 13 which has been shaped into a predetermined non-planar shape.

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15. Use of an aluminium alloy sheet according to claim 14 as an automotive body part.

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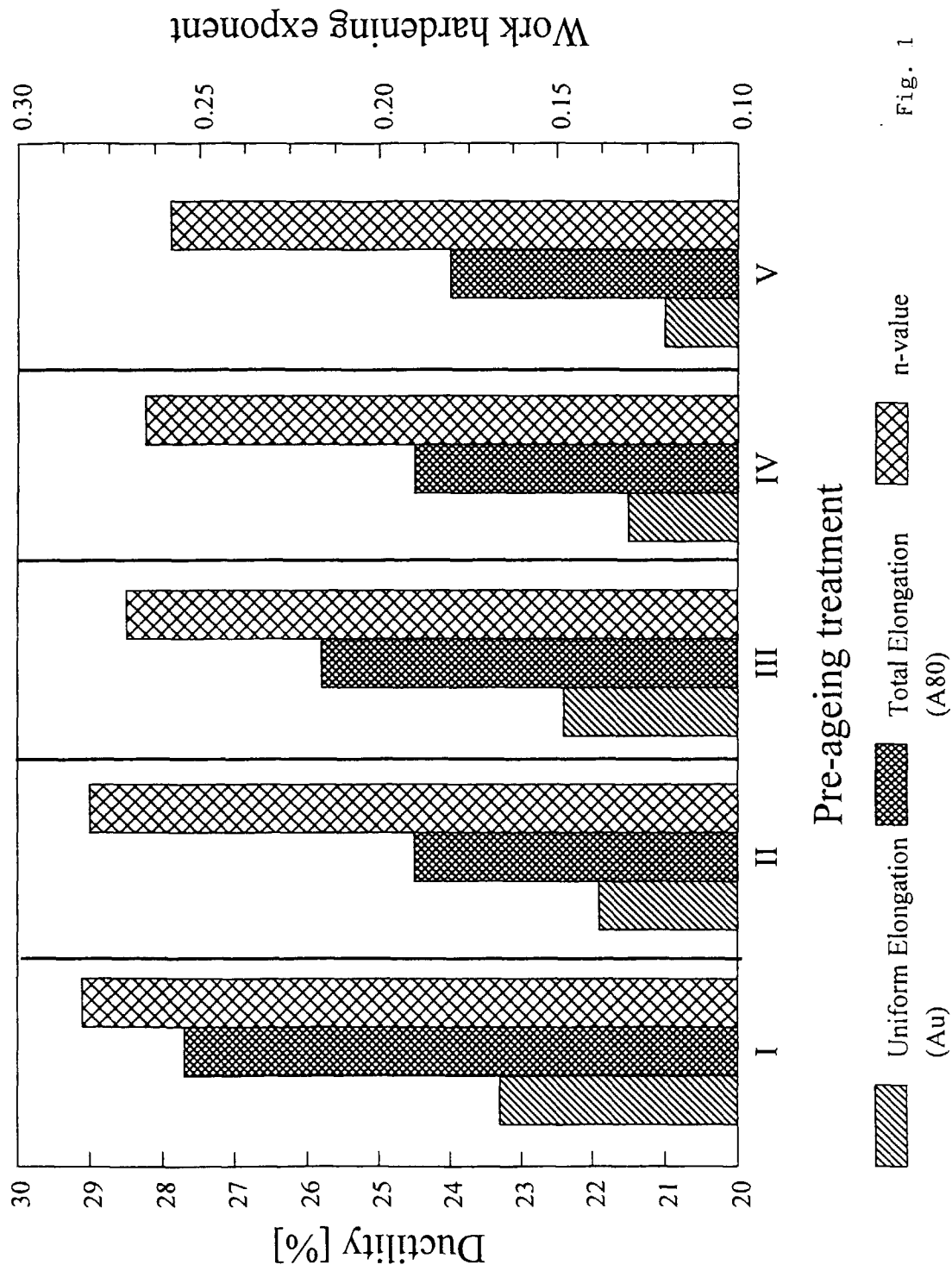


Fig. 1

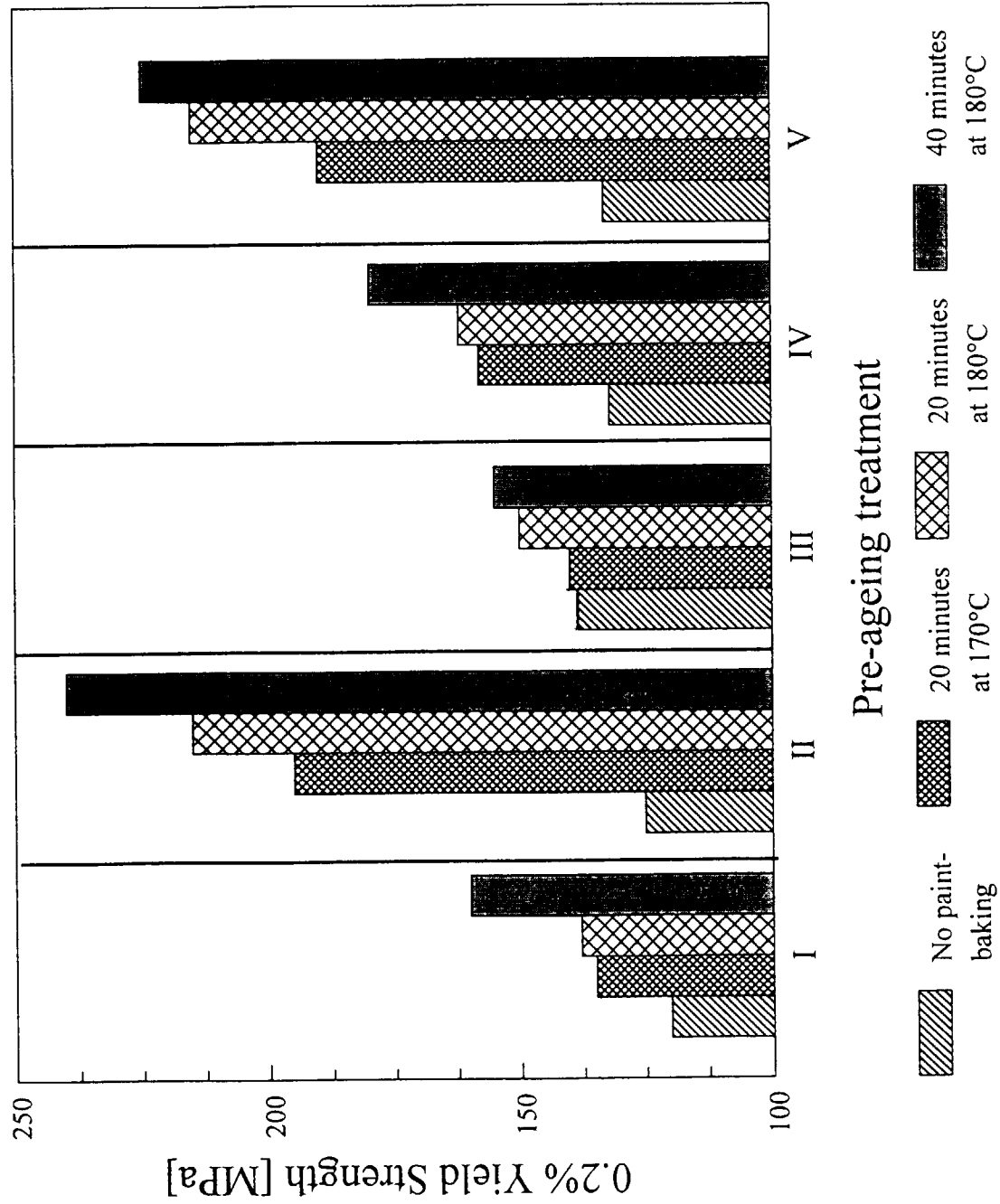
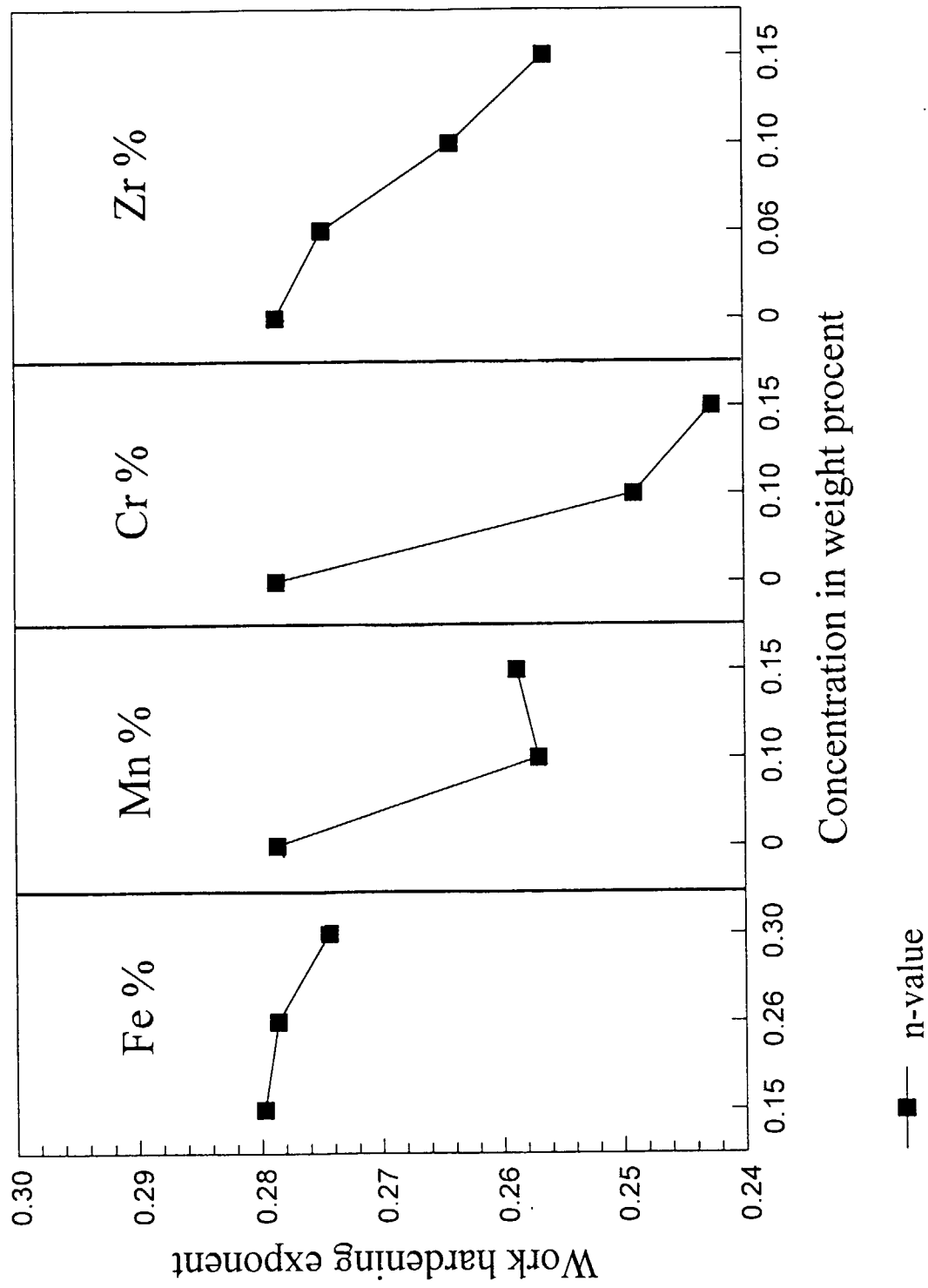


Fig. 2





Annealing for 570°C/10 sec.

Fig. 3

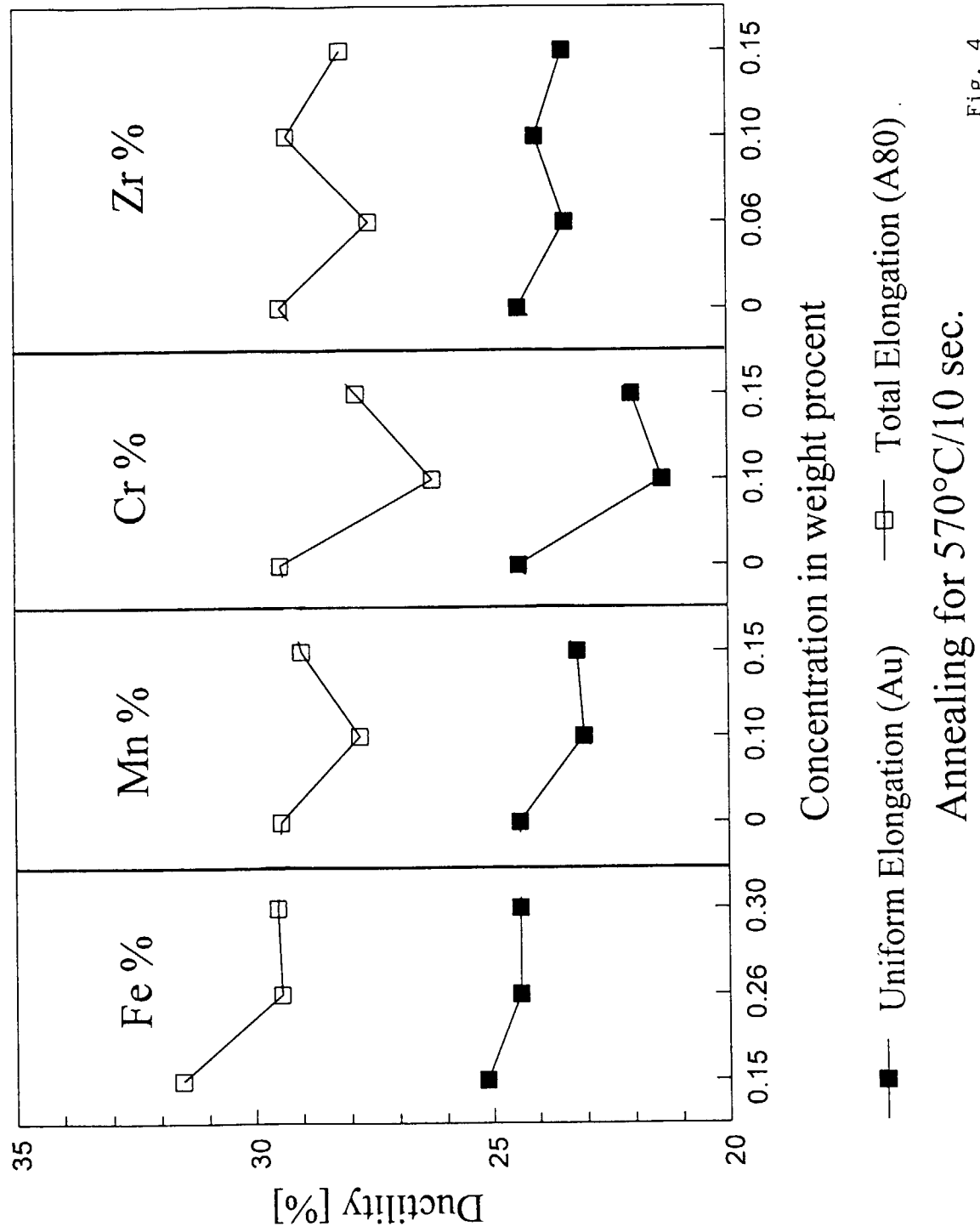


Fig. 4



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## EUROPEAN SEARCH REPORT

Application Number  
EP 97 20 1122

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO 96 07768 A (ALCAN INT LTD ;GUPTA ALOK KUMAR (CA); WHEELER MICHAEL J (CA); BULL) 14 March 1996 * claims 1-7,10-13; table 1 * ---	1-15	C22F1/05 C22F1/043 C22C21/02
X	US 3 135 633 A (J.C. HORNUS)  * column 2, line 9 - line 22 * * claims 1-10; figure 5 * ---	1-7, 10-14	
A	W.HUFNAGEL: "ALUMINIM-SCHLÜSSEL" 1983, ALUMINIUM VERLAG, DÜSSELDORF, DE XP002038066 *ALLOY A-SG* * page 103; table 4.2.1D * ---	1	
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A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 345 (C-1077), 30 June 1993 & JP 05 044000 A (MITSUBISHI ALUM CO LTD), 23 February 1993, * abstract * ---	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6)  C22F C22C
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 505 (C-0775), 5 November 1990 & JP 02 209457 A (KOBEL STEEL LTD), 20 August 1990, * abstract * -----	1	
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>19 August 1997</b>	Examiner <b>Gregg, N</b>
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>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</p> <p>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 ----- &amp; : member of the same patent family, corresponding document</p>			

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