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(54) Aluminium alloy for lithographic sheet

(57) A lithographic sheet obtainable by a method not including an interannealing step is disclosed. The sheet is formed from an alloy having a composition in wt%:

Mg	0.05 to 0.30
Mn	0.05 to 0.25
Fe	0.11 to 0.40
Si	up to 0.25
Ti	up to 0.03
B	up to 0.01
Cu	up to 0.01
Cr	up to 0.03
Zn	up to 0.15

Unavoidable impurities up to 0.05 each, 0.15 total.

Also disclosed is the alloy with a composition as above and a method for forming the lithographic sheet.

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Description

[0001] This invention relates to an Al alloy suitable for processing into a lithographic sheet, which exhibits good mechanical properties with good electrograining characteristics.

[0002] At present the lithographic sheet market largely consists of products in the 1XXX and 3XXX alloy range. During electrograining the 1XXX alloys are used with both nitric and hydrochloric acid electrolytes and generally have the better graining response. The 3XXX alloys, mainly AA3103, are used where greater strength is demanded by the printer but can only be grained in hydrochloric acid, and even then not by all platemakers.

[0003] With the advent of larger, faster presses being used for the high quality end of the market, the Applicants have perceived a need for an alloy for a plate, which combines the good graining response of AA1050A with the strength properties of AA3103.

[0004] Existing alloys such as AA1050A are adversely affected by the "stoving" step used to provide the finished lithographic plate. Stoving has been found to reduce the strength and cause distortion of lithographic sheet material by causing recovery or recrystallisation of the heavily cold worked metal. A useful indication of the likely amount of distortion that may occur is provided by measuring the change in ultimate tensile strength (UTS) or proof strength (PS) caused by stoving. A large loss in strength indicates an unacceptable level of distortion, and difficulties in handling and mounting for use in service.

[0005] Thus, according to the first aspect of the present invention, there is provided an Al alloy suitable for processing into a lithographic sheet, the alloy having a composition in wt%:

Mg	0.05 to 0.30
Mn	0.05 to 0.25
Fe	0.11 to 0.40
Si	up to 0.25
Ti	up to 0.03
B	up to 0.01
Cu	up to 0.01
Cr	up to 0.03
Zn	up to 0.15

[0006] Unavoidable impurities up to 0.05 each, 0.15 total

[0007] Al balance.

[0008] As well as exhibiting good mechanical and electrograining characteristics, the alloy is relatively cheap to produce as it contains alloying elements in smaller amounts compared with AA3103. Furthermore, the alloy has an added commercial benefit by providing the potential for reduced inventories for manufacturers and their customers. The alloy has also been found to resist the softening encountered during stoving or heating at temperatures of about 240°C or even 270°C.

[0009] It is particularly surprising that relatively small amounts of magnesium and manganese are sufficient to attain much improved mechanical properties while still allowing adequate electrograining in hydrochloric acid, and preferably in nitric acid in some embodiments.

[0010] Magnesium is preferably present in an amount of 0.06 to 0.30wt%, even more preferably 0.10 to 0.30-wt%. Magnesium is the element influencing work hardening in the alloy. However, if the magnesium level is raised too far, then electrograining becomes increasingly difficult especially in nitric acid electrolyte.

[0011] Manganese is present in an amount of 0.05 to 0.25wt%, preferably in an amount of 0.05 to 0.20wt%. In either case, the lower limit of Mn may optionally be 0.06wt%. Manganese provides maximum stoved strength, and a minimum drop in strength compared with the as cold rolled sheet. The optimum upper level of manganese is determined by a balance between the desirable stoving resistance on the one hand and the onset of an undesirable level of streaking and discolouration after electrograining on the other hand.

[0012] Preferably, copper is present in an amount up to 0.005%, more preferably up to 0.003%.

[0013] Ti is present in total amounts of up to 0.03wt%. Preferably, up to 0.028wt% of the titanium is free i.e. present in solid solution and not tied up for example as the boride, TiB_2. Preferably, titanium is present in a total amount up to 0.015 wt%, even more preferably 0.010 wt%. Generally, a lower titanium level favours better graining. Grain refiner may or may not be present; if it is, some additional titanium is present over that found in virgin metal. It has been found that if the free titanium content is too high, this may have a detrimental effect on the ability to grain the formed lithographic sheet in nitric acid, although it may still be grainable in hydrochloric acid. The level of titanium preferably needs to be controlled. If too much free titanium is present it is detrimental to graining; titanium combined with boron is not detrimental.

[0014] B is preferably present in an amount up to 0.002.

[0015] In one embodiment, zinc may be present in an amount of up to 0.05wt%. Alternatively, a zinc content in the range of 0.01 to 0.15wt% has been found to be advantageous in order that the alloy can be satisfactorily grained by electrograining in nitric acid. In such an embodiment, the zinc content of the alloy will typically be in the range of from 0.01 to 0.1wt% and more preferably from about 0.01 to 0.08wt%. Especially preferred zinc contents will be in the range of from 0.015 to 0.06wt% and most preferably from about 0.02 to about 0.05wt%.

[0016] Zirconium may typically be present in amounts up to 0.019wt%, for example up to 0.015wt%, particularly up to 0.005wt%. In a preferred embodiment, there is no deliberate addition of zirconium.

[0017] In one embodiment, iron is present in an amount of 0.20 to 0.40%. Silicon may be present in an amount of 0.05 to 0.15%, for example 0.09 to 0.15%. Such alloys have been found to exhibit good strength properties in both the as-rolled and stoved embodiments, and are reasonably cost effective for use in high volume production of lithographic sheet.

[0018] Silicon in solution alters the reactivity of the sheet during electrograining. If the amount of silicon present is too small, too many pits form during graining and the surface is not suitable for lithographic sheet. If the amount of silicon present is too great, too few pits form during electrograining and they are too large.

[0019] Iron in solution has a similar effect to silicon as regards electrograining. In addition, iron forms intermetallic phases present as particles in the sheet. The presence of too many of these iron containing particles is detrimental to graining.

[0020] According to a second aspect of the present invention, there is provided a lithographic sheet formed from the alloy. In such a lithographic sheet, titanium may be present in an amount sufficient to enable the sheet to be capable of being electrograined in nitric acid, although it should be borne in mind that in some embodiments of the invention the presence of titanium is not essential to the ability to electrograin in nitric acid. Preferably, free Ti is present up to 0.028wt% in general but only up to 0.019wt%, for example up to 0.015wt%, for nitric acid graining. TiB_2 is, in one embodiment, present up to 170ppm, but it can be higher.

[0021] According to a further aspect of the present invention, there is provided a DC cast ingot comprising the alloy.

[0022] According to a further aspect of the present invention there is provided a method of processing an Al alloy as defined above, which method comprises the steps of: casting, optional homogenising, optional hot rolling, cold rolling, optional interannealing.

[0023] The casting step is, in one embodiment, a DC casting step. The DC cast ingots are scalped prior to the homogenising step. Homogenising is used to get the right amount of Fe and Mn in solid solution. Other casting options include roll casting or belt casting. If these continuous casting processes are used, then homogenising and scalping may not be necessary. This is because the rapid cooling in continuous casting holds a lot of Fe and Mn in solid solution.

[0024] Heat treatment after casting and before hot rolling affects both the strength loss during stoving and the response to electrograining. To some extent the effects are contradictory and an optimum treatment has to be found. Two alternative homogenising treatments are envisaged. Firstly, there is a two stage homogenisation designated Type 2. This involves slow heating of the alloy to a temperature higher than the rolling temperature and holding at this temperature. During heating to this temperature and during holding, Mn is taken into solution. The ingot is then cooled to the hot rolling temperature and rolled either after holding for a period or immediately on reaching the hot rolling temperature. Some Mn will come out of solution during cooling but the process is slow and most will remain in supersaturated solution. This reduces the strength loss during subsequent stoving but tends to be detrimental to the electrograining response. An example of this treatment is: slow heat to 550 to 610°C and holding in that temperature range for typically 1 to 10 hours. This is followed by cooling to the rolling temperature and hot rolling at a temperature of between 450 to 550°C. Alternatively, the homogenisation may be carried out with a heat-to-roll practice (designated Type 1). This involves heating the alloy as cast (and scalped) to the hot rolling temperature, typically 450 to 550°C, by ramped heating and holding at that temperature for 1 to 16 hours prior to hot rolling. This treatment consumes less energy and take less time than the Type 2 treatment and is therefore less expensive. However, the Type 1 treatment minimises the amount of Mn taken into solution. This benefits electrograining but the strength loss during subsequent stoving is greater. Variations or combinations of these two treatments may be required to achieve the optimum combination of strength after stoving and good electrograining response.

[0025] Where an intermediate annealing step is present, it may be carried out immediately after hot rolling or during cold rolling. The interannealing may be carried out as batch interannealing, in which case it is preferably carried out at 300 to 500°C, for example for 1 to 5 hours. Alternatively, the interannealing may be continuous, in which case it is preferably carried out at 450 to 600°C, preferably for less than 10 minutes, for example for up to 5 minutes, even more preferably up to 1 minute. Preferably, at least forced air quenching is used. It is preferred to cool rapidly in order to hold Mn and Fe in solid solution.

[0026] In one embodiment, the cold roll reduction of the sheet thickness is greater than 30%, preferably greater than 50%.

[0027] An electrograining step may also be provided. Preferably the alloy is capable of being electrograined in hydrochloric acid, even more preferably in both hydrochloric and nitric acids.

[0028] Further steps which may be provided are anodising and stoving. Stoving trials are typically carried out at 240°C for 10 minutes or even 270°C for 10 minutes to harden the photosensitive coating prior to printing. In the Examples below, stoving is simulated by heating the plate to 240°C for 10 minutes or, where noted, to 270°C for 10 minutes. Printers use less time than 10 minutes, typically 3 minutes in continuous ovens, up to 7 minutes in others, and therefore the simulated stoving is a particularly severe test because the degree of softening increases with both time and temperature of stoving. The plate softens via the mechanisms of recovery and recrystallisation of the microstructure and the inherent anisotropy in the plate can lead to off-flatness problems. As mentioned above, the present invention minimises such problems. Generally, as low a drop in proof strength as possible is required.

[0029] According to a further aspect of the present invention, there is provided a method of forming a lithographic sheet comprising electrograining an aluminium metal sheet formed of the above-mentioned alloy in a nitric acid electrolyte until a total charge input of above 82kC/m^2 is applied, wherein the surface of the lithographic sheet comprises a pitted structure. Preferably, the total charge input is about 87kC/m^2. The pitted structure may provide total coverage of the surface of the material and sufficient roughness to allow good adhesion of a light-sensitive coating, together with good wear resistance and water retention following anodising and post anodic treatment.

[0030] The invention will now be described with reference to, and as illustrated in, the accompanying drawings, and in which:

Figures 1 a and 1b show, respectively, the proof strength and ultimate tensile strength at final gauge in the as-rolled (H18 - that is with an interanneal) condition and after stoving for Mg or Mn additions;
Figures 2a and 2b show, respectively, the proof strength and ultimate tensile strength at final gauge in the as rolled condition and after stoving for other Mg and/or Mn additions;
Figures 3a and 3b show similar properties in the H19 condition (without interanneal);
Figures 4a to 4d show proof strength and nitric acid graining response for various alloy compositions for different homogenising and annealing conditions;
Figures 5a and 5b show, respectively, the proof strength and ultimate tensile strength for various treatments in the H18 condition against <u>total</u> Ti content;
Figures 6a and 6b show similar properties in the H19 condition;
Figure 7 shows the ultimate tensile strength of various alloys under varying treatment conditions;
Figure 8 shows the ultimate tensile strength of various alloys under various treatment conditions against the annealing temperature.
Figures 9a - c show the softening behaviour of various alloys against stoving temperature.

<u>EXAMPLE 1 (Comparative)</u>

[0031] A series of alloys based on the standard AA1050A composition were cast, rolled and electrograined in the laboratory to see the effects of single additions of various elements on tensile properties and electrograining response. The compositions used are shown in Table 1:

<u>TABLE 1. Composition and TEP for Alloy trials of AA1050A + Mn or Mg</u>

Cast ID	Si	Fe	Mn	Mg	Total Ti	Free Ti*	B
Std	0.08	0.30	<0.003	<0.001	0.006	0.003	0.0012
Std+Mg0.01	0.08	0.30	<0.003	0.010	0.006	0.004	0.0010
Std+Mg0.02	0.08	0.30	<0.003	0.020	0.006	0.004	0.0010
Std+Mg0.3	0.08	0.30	<0.003	0.300	0.008	0.003	0.0022
Std+Mn0.1	0.08	0.30	0.100	<0.001	0.006	0.004	0.0011
Std+Mn0.2	0.08	0.30	0.200	<0.001	0.007	0.004	0.0012
Std+Mn0.5	0.08	0.30	0.500	<0.001	0.006	0.003	0.0013
Zn, Cu, Cr and Zr all = 0.001 wt% for all variants shown in Table 1. *Free Ti is the Ti in the Al solid solution and not including Ti combined with B as TiB_2 particles.							

[0032] Compositions given in Table 1 are rounded to the nearest significant figure and Std means typical AA1050A with the compositions shown.

[0033] Rolling blocks approximately 70mm thick by 180mm wide by 200mm long were scalped from ingots cast in large book moulds. The rolling blocks were homogenised by heating slowly to 600°C and holding for several hours followed by a 2 hour cool to 500°C for 10 hours to allow equilibration of solute to occur, prior to hot rolling. This two-stage homogenisation is an example of a Type 2 pre-heat. The rolling blocks were hot rolled to an intermediate gauge of about 9mm with a finish temperature of about 150°C and allowed to air cool. Subsequent cold rolling to a final gauge of 0.3mm was done with an intermediate anneal at about 2mm gauge by heating to 450°C and holding for 2 hours. The tensile properties of the final gauge sheet, before and after a simulated stoving treatment for 10 minutes at 240°C, were measured in the longitudinal and transverse orientations (with respect to the rolling direction).

[0034] Figures 1 a and 1b show, respectively, the proof strength and tensile strength at final gauge in the as rolled (H18) condition and after stoving for the Mn and Mg additions. It can be seen that even small Mg additions give significant work hardening effect and thus a higher as rolled strength. However on stoving the drop in strength is also large. The maximum stoved strength (and minimum drop in strength) is seen in the Mn containing alloys.

EXAMPLE 2

[0035] Further experiments were carried out to investigate a wider range of Mg and Mn additions in combination.

[0036] A series of cast book mould alloys are shown in Table 2:

TABLE 2. AA1050A+Mg+Mn Alloy Trials

Cast ID	Si	Fe	Mn	Mg	Total Ti	Free Ti*	Zn	B
Std	0.08	0.30	<0.003	<0.001	0.006	0.003	0.006	0.0012
0.1Mg0.1Mn	0.08	0.30	0.100	0.100	0.006	0.003	0.006	0.0013
0.1Mg0.5Mn	0.08	0.30	0.500	0.100	0.006	0.003	0.006	0.0015
0.3Mg0.1Mn	0.08	0.30	0.100	0.300	0.006	0.002	0.006	0.0019
1.0Mg0.1Mn	0.08	0.30	0.100	1.000	0.006	0.002	0.006	0.0017
Cu, Cr and Zr all = 0.001 wt% for all variants shown in Table 2. *Free Ti is the Ti in the Al solid solution and not including Ti combined with B as TiB_2 particles.								

[0037] Compositions given in Table 2 are rounded to the nearest significant figure and Std means typical AA1050A with the additions shown.

[0038] Rolling blocks were manufactured in a similar manner to that described in Example 1. In addition to the standard two-stage preheat (Type 2) described above, a set of blocks were homogenised with a heat-to-roll practice (Type 1). This consists of a ramped heating to the rolling temperature of 500°C and holding for a few hours (total heating cycle about 16 hours). The blocks were either rolled to final gauge with an interanneal, as above, to give material in the H18 condition, or without any interanneal to give material in the H19 condition. The H19 route is more economical while the H18 route gives an opportunity to control solute and grain structure, and hence stoving response and surface streakiness in the final gauge product.

[0039] The mechanical properties of these materials at final gauge, before and after the stoving treatment, are shown in Figures 2 (H18) and 3 (H19). It can be seen that for most compositions the H 18 strength after stoving is lower than for the H19 material.

[0040] Other conclusions are:

- Pre-heat Type 1 in general gives lower stoved strength as compared with pre-heat Type 2
- H19 treatment gives consistently higher as-rolled strength; and
- Type 2 pre-heat results in the lowest drop during softening. This is consistent with the recovery being controlled via solute rather than dispersoids.

EXAMPLE 3

[0041] Final gauge samples prepared in a similar manner to that described in Examples 1 and 2 and from the same casts were pre-cleaned in a 3% sodium hydroxide solution at 60°C for 10 seconds and grained in a laboratory twin cell system operated in the liquid contact mode. The electrolyte was 1% nitric acid. The voltage applied was 14V AC (conventional sine wave source). The spacing between each electrode was 15mm and the counter electrodes were conventional impregnated graphite used industrially. This arrangement has been shown to produce surfaces similar to those produced commercially using standard 1050A lithographic quality material. The time taken to produce a fully grained surface on such a material is approximately 30 seconds and the total charge input is about 87kC/m^2. Due to the symmetrical nature of the arrangement the forward and reverse current density is approximately equal.

[0042] The electrograining response of these materials in nitric acid is indicated in Table 3:

TABLE 3. Laboratory Nitric Acid Graining Trials

%Mg	%Mn	H18 Type 1	H18 Type 2	H19 Type 1	H19 Type 2
0.000	0.001	✔ ✔	✔ ✔	✔	✔
0.000	0.10	✔ ✔	✔ ✔	✔	✔
0.000	0.20	✔ ✔	✔ ✔	✔	×
0.000	0.50	✔	×	×	×
0.10	0.10	✔	✔	✔	✔
0.10	0.50	×	×	×	×
0.30	0.001	✔	✔	✔	✔
0.30	0.10	✔	✔	✔	✔
1.00	0.10	✔	✔	×	×

✔ ✔ Good
✔ Acceptable
× Unacceptable
×× poor

[0043] Figures 4a to 4d illustrate property-electrograining maps for homogenising treatments Type 1 and Type 2 in the H18 or H19 condition. Figures 4a and 4b show graining and proof strength results after stoving for 10 minutes at 240°C for Type 1 and Type 2 homogenisation respectively in H18 conditions. Figures 4c and 4d show similar results for Type 1 and 2 homogenisation respectively in the H19 condition. There is sufficient overlap between the good strength properties and the good graining response in the alloy range tested.

EXAMPLE 4

[0044] Ti is an important element in electrograining response in nitric acid. So a middle level Mn/Mg variant was chosen and ingots were cast with a range of Ti levels, as shown in Table 4 and heat treated and rolled as in Example 2:

TABLE 4. Ti Unialloy Variants

Wt% Mg	Wt% Mn	Wt% B	Wt% Ti (total)	Wt% free Ti*
0.10	0.10	0.0011	0.010	0.008
0.10	0.10	0.0011	0.013	0.011
0.10	0.10	0.0012	0.018	0.015
0.10	0.10	0.0011	0.021	0.019

Cu, Cr and Zr all = 0.001 wt% for all variants shown in Table 4.
*Ti in the Al solid solution and not including Ti combined with B as TiB_2 particles.

[0045] Figures 5 and 6 show that the strength values of this system are almost independent of Ti within the range of levels explored (with the exception of <100ppm Ti for the H19 Type 2 preheat variant). The following conclusions can be made:

- Type 2 pre-heat gives higher strength, most notably for H19 samples; and
- The very slight extra strength attained by the H19 samples with Ti > 100ppm is due to the extra cold reduction used to investigate differences between the experimental and anticipated commercial rolling schedules (0.3mm compared with 0.7mm).

[0046] The graining response is shown in Table 5:

TABLE 5. Ti Unialloy Variants Nitric Acid Graining Response

%Ti (total)	H18 Type 1	H18 Type 2	H19 Type 1	H19 Type 2
0.006	✔ ✔	✔ ✔	✔ ✔	✔ ✔
0.010	✔ ✔	✔ ✔	✔ ✔	×
0.013	✔ ✔	✔	×	×
0.018	✔	×	×	×
0.021	×	×	×	× ×

[0047] Generally a lower free Ti level favours better graining.

EXAMPLE 5

[0048] Commercial scale trials have been carried out as follows:
Two trials have been carried out with the alloys listed in Table 6. The existing litho alloys are included for comparison. Ingots of these alloys were DC cast measuring 4250mm long by 1300mm wide and 600mm deep and were scalped. Homogenising before hot rolling was Type 2, in this case the ingot was heated to 600°C±10°C for about 4 hours and then cooled to 500°±10°C and hot rolled.
Material destined to be in the H18 condition was hot rolled to 4.2 mm and then cold rolled to a final gauge of 0.28 mm with an interanneal at about 2.2 mm. Material destined to be in the H19 condition was hot rolled to 3.5 mm and then cold rolled to a final gauge of 0.28 mm without an inter-anneal.

TABLE 6. Commercial Unialloy Trials Alloy Composition

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	B
AA3103 (AlMn1)	0.00-0.50	0.0-0.7	0.00-0.10	0.9-1.5	0.00-0.30	0.00-0.10	0.00-0.20		
AA1050A (Al99.5)	0.00-0.25	0.00-0.40	0.00-0.05	0.00-0.05	0.00-0.05		0.00-0.07	0.00-0.05	
1st version	0.08	0.34	0.001	0.19	0.06	0.001	0.008	0.013	0.0007
2nd version	0.08	0.32	0.001	0.10	0.13	0.001	0.006	0.013	0.0006
3rd version	0.09	0.33		0.06	0.19	0.001	0.006	0.016	0.0011
4th version	0.09	0.32		0.10	0.14	0.001	0.006	0.004	0.0006
5th version	0.08	0.33	0.001	0.09	0.08		0.020	0.009	0.0005
6th version	0.08	0.32		0.10	0.13		0.021	0.006	0.0007

[0049] Mechanical properties of these alloys are shown in Figure 7 and again show that the new alloy (in all variants) in the H19 condition has high strength after stoving.

EXAMPLE 6

[0050] Figure 8 shows that the final gauge stoving response of the alloy labelled 1st version in Table 6 is independent of the interannealing temperature compared to the AA1050A alloy. This is consistent with the stoving resistance being controlled by manganese in solid solution, which has a high solid solubility over this temperature range. Fe has a very low solubility resulting in a high driving force for Fe precipitation during inter-anneal. Consequently a high interannealing temperature is usually used to keep Fe solute levels high in the AA1050A product. An advantage of the new alloy is that it could be supplied in the H18 condition for intermediate strength applications by using a relatively low inter-anneal temperature thus saving production costs.

[0051] The 1st version in Table 6 was tested against normal plates, of which typically 4% fail due to plate breakage. With a sample of 3,500 plates, only 1.5% failed for this reason; a marked improvement.

[0052] All of the versions in Table 6 have been trialled for both nitric and hydrochloric acid electrolytes and the graining and mechanical properties were found to be acceptable. This is another surprising advantage over AA1050A, which is often prone to streaky electrograining defects when supplied in the H19 condition.

EXAMPLE 7

[0053] A further series of commercial alloys were cast, homogenised and rolled using the conditions described in Example 5. The compositions used are shown in Table 7.

[0054] The blocks were either rolled to final gauge with an interanneal, as above, to give material in the H18 condition, or without interanneal to give material in the H19 condition. Stoving was carried out for 10 minutes at various temperatures to simulate the actions of a printer and the results are shown in Figures 9a - c. From this it can be seen that material in the H19 condition for the alloys shown has a higher strength than in the H18 condition. At higher baking temperatures the material containing Mn in the H19 condition has much better mechanical properties than the comparison material in a similar condition.

TABLE 7

Sample	Si	Fe	Cu	Mn	Mg	Zn	Ti	B
OQ 3051 H18 (H502)	0.08	0.3	0.001	0.05	0.18	0.007	0.014	0.0003
OQ 3051 H19 (H502)	0.08	0.3	0.001	0.05	0.18	0.008	0.015	0.0004
Comparison	0.07	0.35	0.002	0.002	0.18	0.006	0.005	0.0007

EXAMPLE 8

[0055] Alloys having the compositions I, II and III as set out below were formed into sheet materials in the same manner as Example 1 and experiments were carried out to investigate the electrograining response in nitric acid.

TABLE 8

Alloy Compositions

	I	II	III
B	0.0016	0.0015	0.0014
Mg	0.100	0.100	0.100
Mn	0.100	0.100	0.100
Zn	0.005	0.022	0.051
Fe	0.30	0.30	0.30
Si	0.08	0.08	0.08
Ti	0.007	0.006	0.006

Table continued

	Alloy Compositions		
Cu and Cr	0.001	0.001	0.001
Al	balance	balance	balance

Electrograining

[0056] A further set of samples of sheet formed from compositions I, II and III were prepared using a Type 2 homogenisation and were electrograined as described in Example 3 with the exception that the voltage applied was lower than standard, in order to demonstrate the sensitivity.

[0057] The surfaces of the samples after electrograining were subjected to visual inspection to assess the graining response. The results are shown in Table 9. All samples grained with the reduced voltage had the same amount of charge passed.

TABLE 9

Electrograining Voltage	Alloy Composition		
	I	II	III
14V	√	√√	√√
13V	X	√√	√√
12V	X	0	√√
11V	X	X	0

Key
X = poor
0 = borderline acceptability
√ = acceptable
√ = good

[0058] The results demonstrate that by incorporating zinc into the alloy at 0.02 and 0.05wt% additions improves the graining response in H19 (with Type 2 homogenisation) condition.

Claims

1. A lithographic sheet formed from an alloy, the alloy having a composition in wt%:

Mg	0.05 to 0.30
Mn	0.05 to 0.25
Fe	0.11 to 0.40
Si	up to 0.25
Ti	up to 0.03
B	up to 0.01
Cu	up to 0.01
Cr	up to 0.03
Zn	up to 0.15

Unavoidable impurities up to 0.05 each, 0.15 total
Al balance,
wherein the lithographic sheet is obtainable by a method which does not comprise an interannealing step.

2. A lithographic sheet according to claim 1, wherein Mg is present in an amount of 0.06 to 0.30wt%.

3. A lithographic sheet according to claim 2, wherein Mg is present in an amount of 0.10 to 0.30wt%.

4. A lithographic sheet according to any preceding claim, wherein Mn is present in an amount of 0.05 to 0.20wt%.

5. A lithographic sheet according to any preceding claim, wherein up to 0.028wt% free Ti is present.

6. A lithographic sheet according to any preceding claim, wherein Ti is present in a total amount up to 0.015wt%.

7. A lithographic sheet according to claim 6, wherein Ti is present in a total amount up to 0.010wt%.

8. A lithographic sheet according to any preceding claim, wherein up to 0.019wt% Zr is present.

9. A lithographic sheet according to claim 8, wherein up to 0.005wt% Zr is present.

10. A lithographic sheet according to any preceding claim, wherein there is no deliberate addition of Zr.

11. A lithographic sheet according to any preceding claim, wherein Fe is present in an amount of about 0.20 to 0.40wt%.

12. A lithographic sheet according to any preceding claim, wherein Si is present in an amount of about 0.05 to 0.15wt%.

13. A lithographic sheet according to any preceding claim, wherein Si is present in an amount of 0.09 to 0.15wt%.

14. A lithographic sheet according to any preceding claim, wherein Zn is present in an amount of 0.05wt%.

15. A lithographic sheet according to any one of claims 1 to 13, wherein Zn is present in an amount of 0.01 to 0.1wt%.

16. A lithographic sheet according to claim 15, wherein Zn is present in an amount of from 0.015 to 0.06wt%.

17. A lithographic sheet according to claim 16, wherein Zn is present in an amount of from about 0.02 to about 0.05wt%.

18. A lithographic sheet according to any one of the preceding claims,
wherein Ti is present in an amount sufficient to enable the sheet to be capable of being electrograined in nitric acid.

19. A method of forming a lithographic sheet according to any one of claims 1 to 18, which method comprises the steps of: casting, optional homogenising, optional hot rolling, cold rolling, and which does not comprise interannealing.

20. A method according to claim 19, wherein the casting step is carried out by DC casting.

21. A method according to claim 19 or 20, wherein the homogenisation step is carried out by heating the cast alloy to a temperature of 550 to 610°C for 1 to 10 hours and subsequently cooling to a hot rolling temperature of between 450 and 550°C.

22. A method according to claim 19 or 20, wherein the homogenisation step is carried out by ramped heating of the cast alloy to a temperature of 450 to 550°C for 1 to 16 hours and subsequently hot rolling at that temperature.

23. A method according to any one of claims 19 to 22, further comprising the step of electrograining.

24. A method according to claim 23, wherein the alloy is electrograined in hydrochloric acid.

25. A method according to claim 23, wherein the alloy is electrograined in nitric acid.

26. A method according to claim 23, wherein the alloy is capable of being electrograined in both hydrochloric and nitric acids.

27. A method of forming a lithographic sheet comprising electrograining an aluminium metal sheet in a nitric acid electrolyte until a total charge input of above $82kC/m^2$ is applied, wherein the surface of the lithographic sheet comprises a pitted structure, and wherein the lithographic sheet is formed according to any one of claims 1 to 18.

28. A method according to claim 27, wherein a total charge input of about $87kC/m^2$ is applied.

29. An Al alloy suitable for processing into a lithographic sheet, the alloy having a composition in wt%:

Mg	0.05 to 0.30
Mn	0.05 to 0.25
Fe	0.11 to 0.40
Si	up to 0.25
Ti	up to 0.03
B	up to 0.01
Cu	up to 0.01
Cr	up to 0.03
Zn	up to 0.15

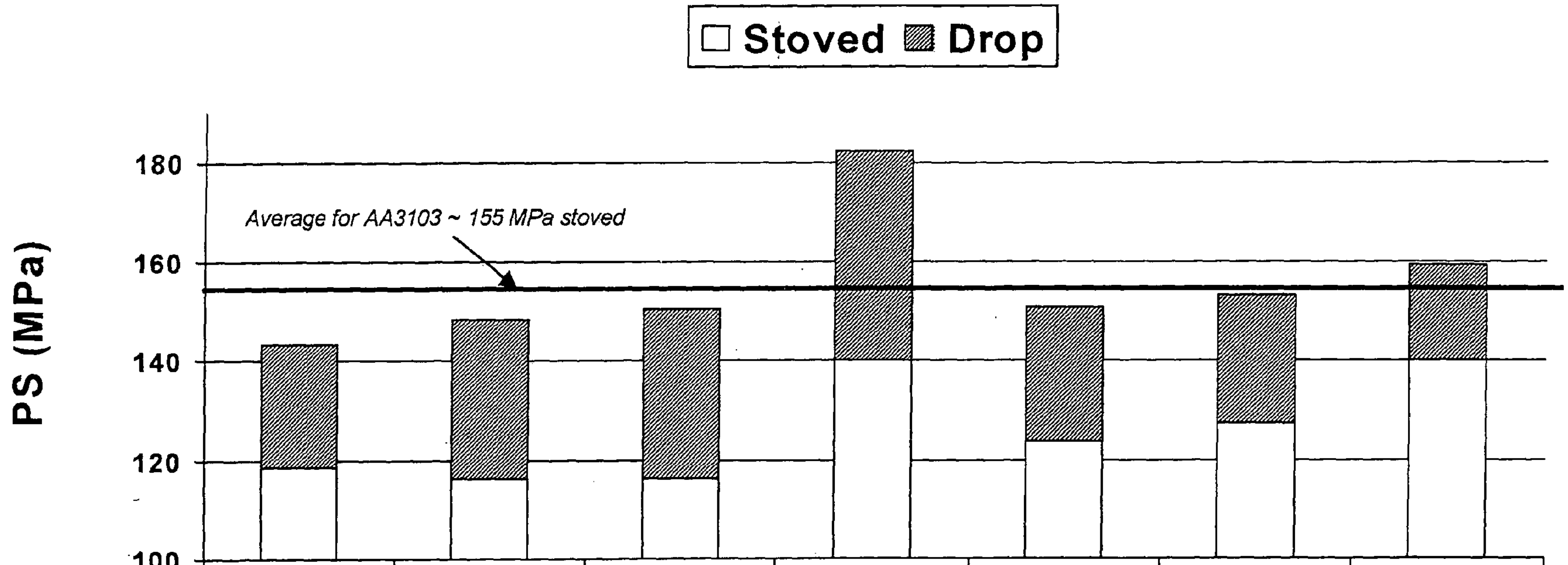
Unavoidable impurities up to 0.05 each, 0.15 total
Al balance.

30. An Al alloy according to claim 29 having a composition in wt%:

Mg	0.10
Mn	0.10
Zn	0.02 to 0.05
Fe	0.30
Si	0.08
Ti	0.006

Unavoidable impurities up to 0.05 each, 0.15 total
Al balance.

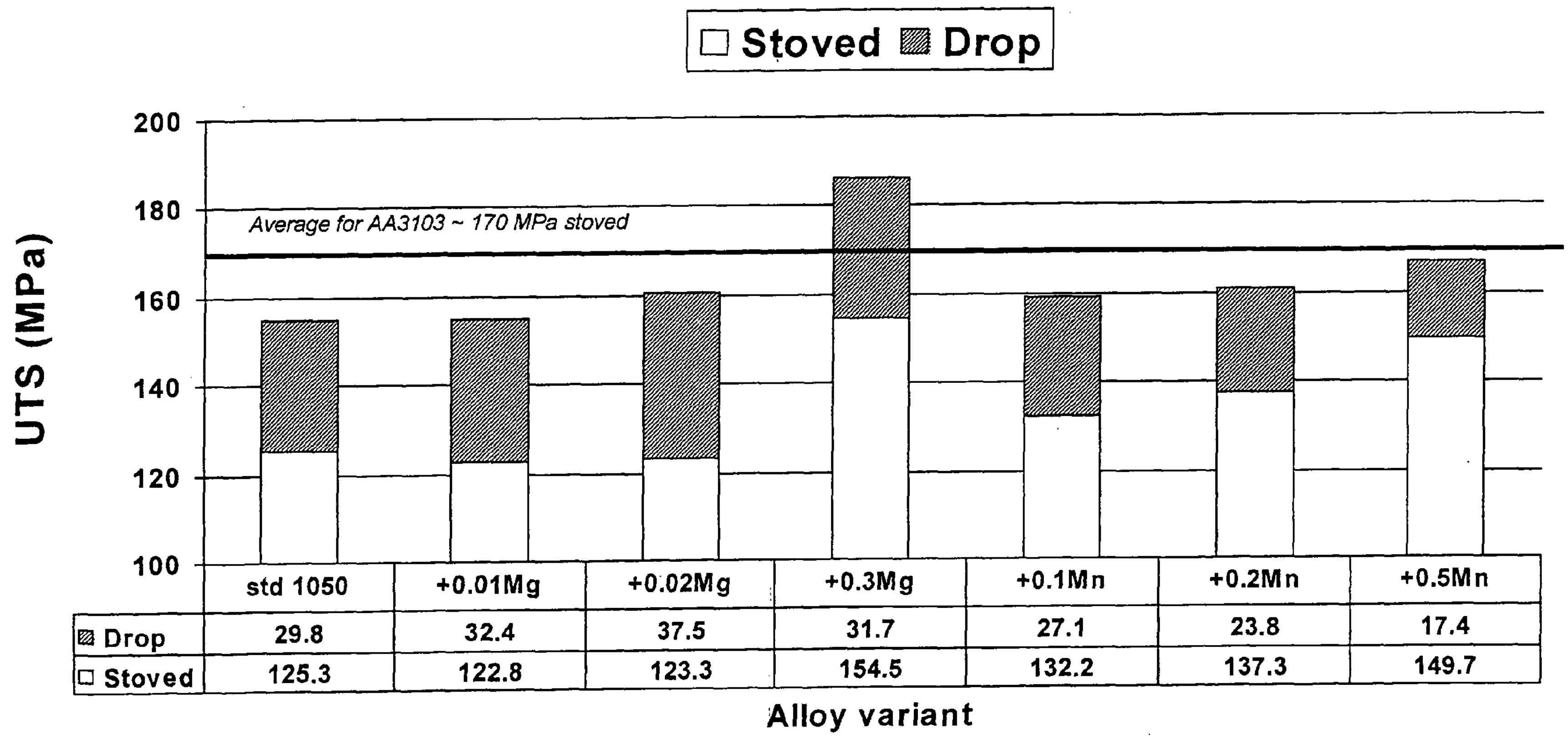
Figure 1a Preheat type-2, H18.



	std 1050	+0.01Mg	+0.02Mg	+0.3Mg	+0.1Mn	+0.2Mn	+0.5Mn
Drop	25	32.4	34.5	42	27.3	25.9	19.4
Stoved	118.6	116.3	116.1	140.1	123.7	127.2	140

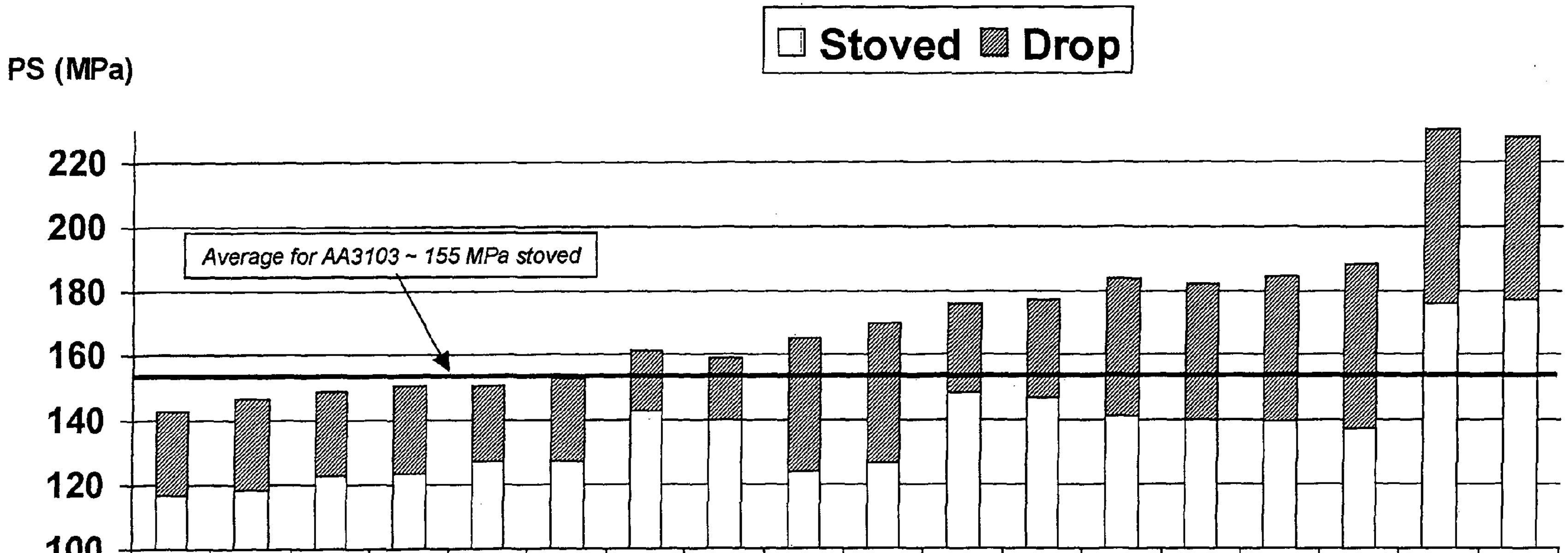
Alloy variant

Figure 1b Preheat type-2, H18.



	std 1050	+0.01Mg	+0.02Mg	+0.3Mg	+0.1Mn	+0.2Mn	+0.5Mn
Drop	29.8	32.4	37.5	31.7	27.1	23.8	17.4
Stoved	125.3	122.8	123.3	154.5	132.2	137.3	149.7

Figure 2a

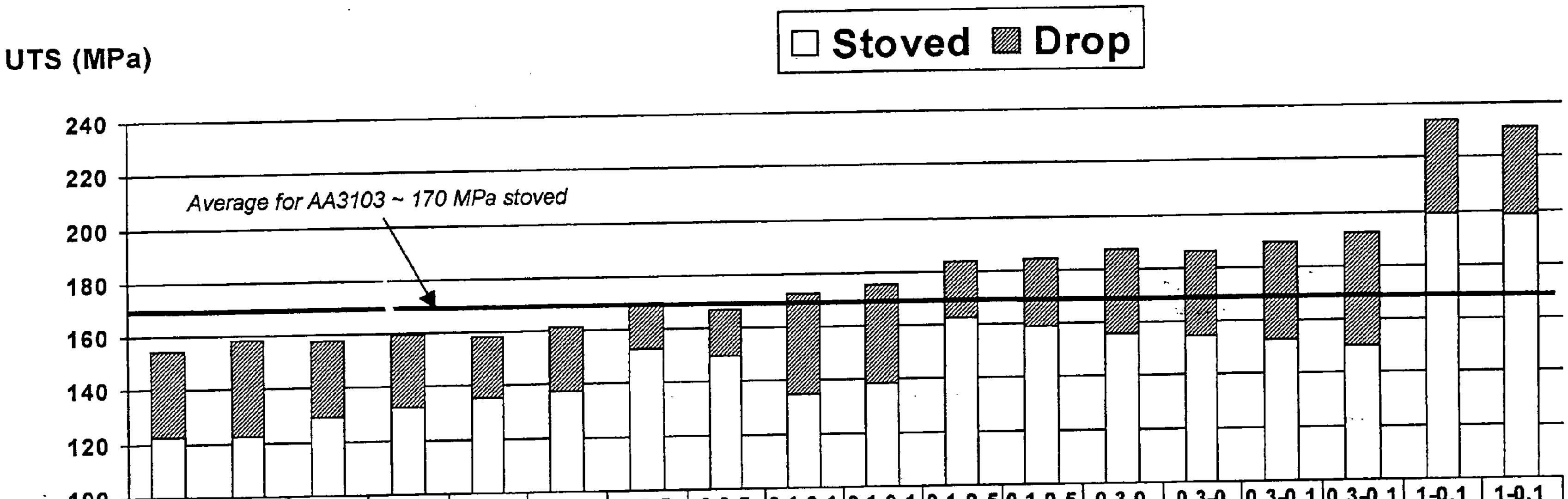


*, †	0-0 1	0-0 2	0-0.1 1	0-0.1 2	0-0.2 1	0-0.2 2	0-0.5 1	0-0.5 2	0.1-0.1 1	0.1-0.1 2	0.1-0.5 1	0.1-0.5 2	0.3-0 1	0.3-0 2	0.3-0.1 1	0.3-0.1 2	1-0.1 1	1-0.1 2
Drop	26	28.6	26.3	27.3	23.2	25.9	18.1	19.4	41.7	43	27.5	30.4	42.3	42	44.9	50.6	54	51.2
Stoved	116.7	118.3	122.8	123.7	127.4	127.2	143.1	140	123.8	126.6	148.5	146.8	141.3	140.1	139.4	137.4	176	176.8

* %Mg-%Mn

† Pre-heat (type 1 or 2 see text)

Figure 2b

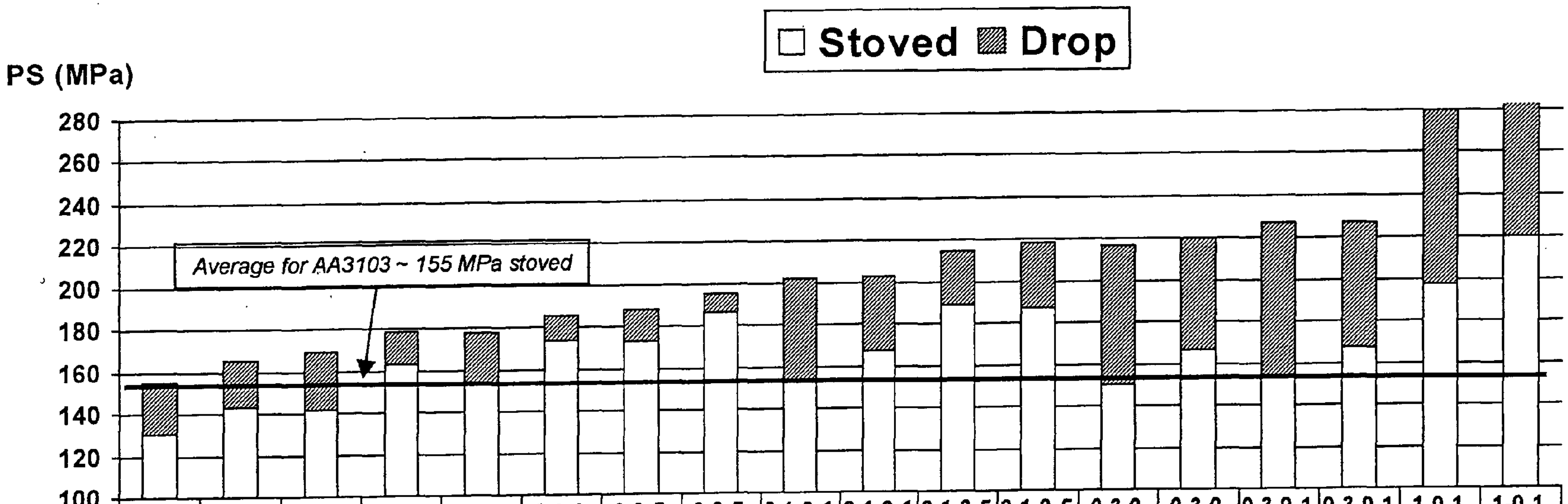


	* 0-0 † 1	0-0 2	0-0.1 1	0-0.1 2	0-0.2 1	0-0.2 2	0-0.5 1	0-0.5 2	0.1-0.1 1	0.1-0.1 2	0.1-0.5 1	0.1-0.5 2	0.3-0 1	0.3-0 2	0.3-0.1 1	0.3-0.1 2	1-0.1 1	1-0.1 2
Drop	32.4	35.8	28.1	27.1	22.9	23.8	16.2	17.4	37.6	37.2	21.1	25.3	31.6	31.7	36.7	42.2	34.2	32.6
Stoved	122.4	122.4	129.3	132.2	135.5	137.3	152.8	149.7	134.9	138.2	162.3	159	156	154.5	152.5	150.4	199.3	198.2

* %Mg-%Mn

† Pre-heat (type 1 or 2 see text)

Figure 3a

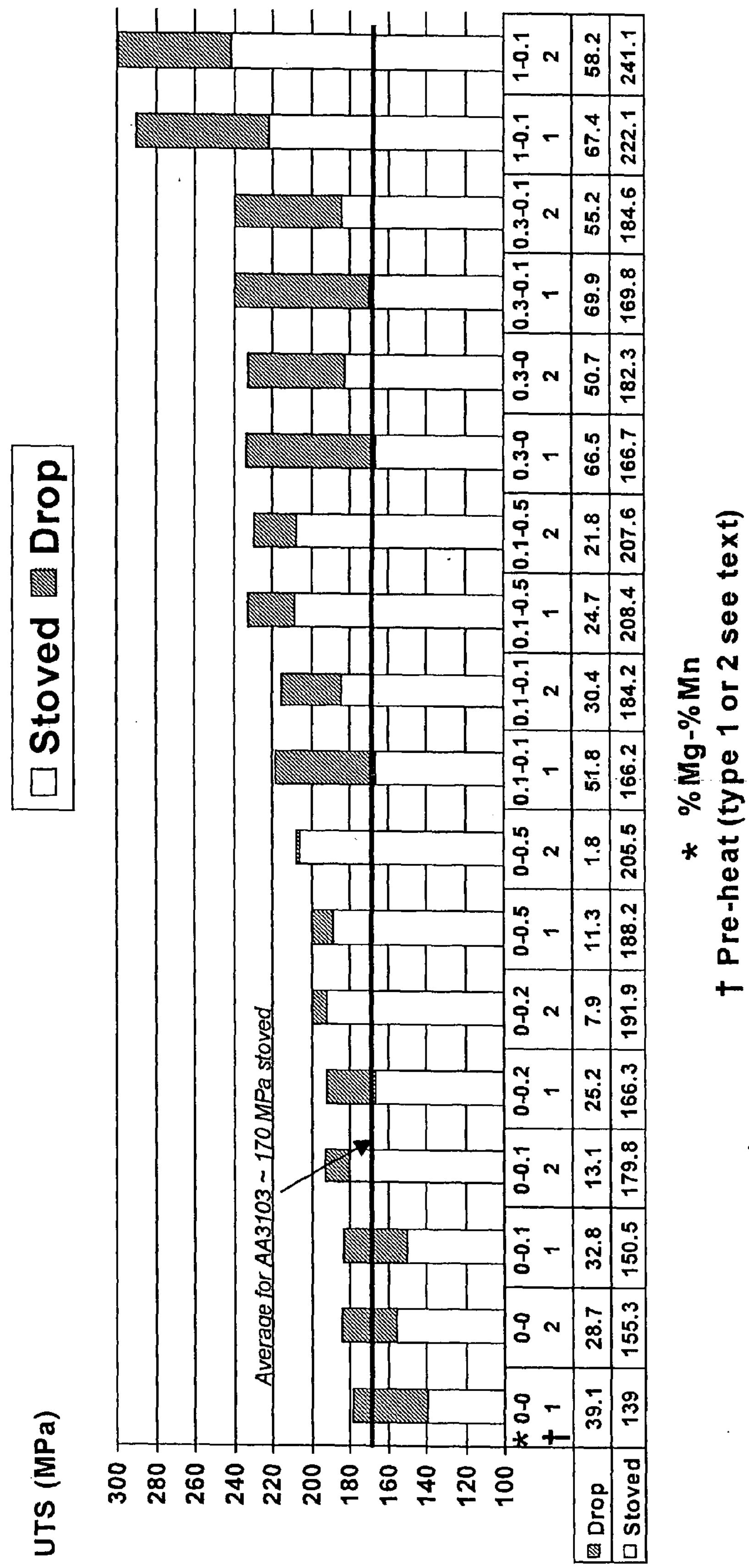


	*0-0 †1	0-0 2	0-0.1 1	0-0.1 2	0-0.2 1	0-0.2 2	0-0.5 1	0-0.5 2	0.1-0.1 1	0.1-0.1 2	0.1-0.5 1	0.1-0.5 2	0.3-0 1	0.3-0 2	0.3-0.1 1	0.3-0.1 2	1-0.1 1	1-0.1 2
Drop	25.1	21.5	27.6	15.5	24	11.8	15.1	8.3	49.1	35.6	25.9	31.1	66.9	54	73.6	59.9	82.4	71.7
Stoved	130.3	143.5	141.9	163	153.6	174	172.8	186.5	153.4	167.6	188.8	187.6	150.6	166.5	153.7	167.5	197.8	220.2

* % Mg-% Mn

† Pre-heat (type 1 ro 2 see text)

Figure 3b



*	0-0	0-0	0-0.1	0-0.1	0-0.2	0-0.2	0-0.5	0-0.5	0.1-0.1	0.1-0.1	0.1-0.5	0.1-0.5	0.3-0	0.3-0	0.3-0.1	0.3-0.1	1-0.1	1-0.1
†	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Drop	39.1	28.7	32.8	13.1	25.2	7.9	11.3	1.8	51.8	30.4	24.7	21.8	66.5	50.7	69.9	55.2	67.4	58.2
Stoved	139	155.3	150.5	179.8	166.3	191.9	188.2	205.5	166.2	184.2	208.4	207.6	166.7	182.3	169.8	184.6	222.1	241.1

Figure 4a Pre-heat type-1, H18

		Mg					
	AA1050 +	0	0.01	0.02	0.1	0.3	1.0
Mn	0	✔ ✔				✔	
	0.1	✔ ✔			✔	✔	✔
	0.2	✔ ✔					
	0.5	✔			✕		

Key	Stoved PS
	No test
	<130
	130-140
	140-150
	150-160
	>160

Nitric Acid Graining Response: ✕✕=Poor. ✕=Unacceptable. ✔ = Acceptable. ✔ ✔ =Good.

Figure 4b Pre-heat type-2, H18

		Mg					
	AA1050 +	0	0.01	0.02	0.1	0.3	1.0
Mn	0	✓✓	✓✓	✓✓		✓	
	0.1	✓✓			✓	✓	✓
	0.2	✓✓					
	0.5	✕			✕		

Key	Stoved PS
	No test
	<130
	130-140
	140-150
	150-160
	>160

Nitric Acid Graining Response: ✕✕=Poor. ✕=Unacceptable. ✓ = Acceptable. ✓✓=Good.

Figure 4c Pre-heat type-1, H19

	AA1050 +	Mg 0	Mg 0.01	Mg 0.02	Mg 0.1	Mg 0.3	Mg 1.0
Mn	0	✓				✓	
	0.1	✓			✓	✓	✗
	0.2	✓					
	0.5	✗			✗		

Key	Stoved PS
	No test
	<130
	130-140
	140-150
	150-160
	>160

Nitric Acid Graining Response: ✗✗=Poor. ✗=Unacceptable. ✓ = Acceptable. ✓ ✓ =Good.

Figure 4d Pre-heat type-2, H19

		Mg					
	AA1050 +	0	0.01	0.02	0.1	0.3	1.0
Mn	0	✓	✓	✓		✓	
	0.1	✓			✓	✓	✗
	0.2	✗					
	0.5	✗			✗		

Key	Stoved PS
	No test
	<130
	130-140
	140-150
	150-160
	>160

Nitric Acid Graining Response: ✗✗=Poor. ✗=Unacceptable. ✓ = Acceptable. ✓✓ =Good.

Figure 5a

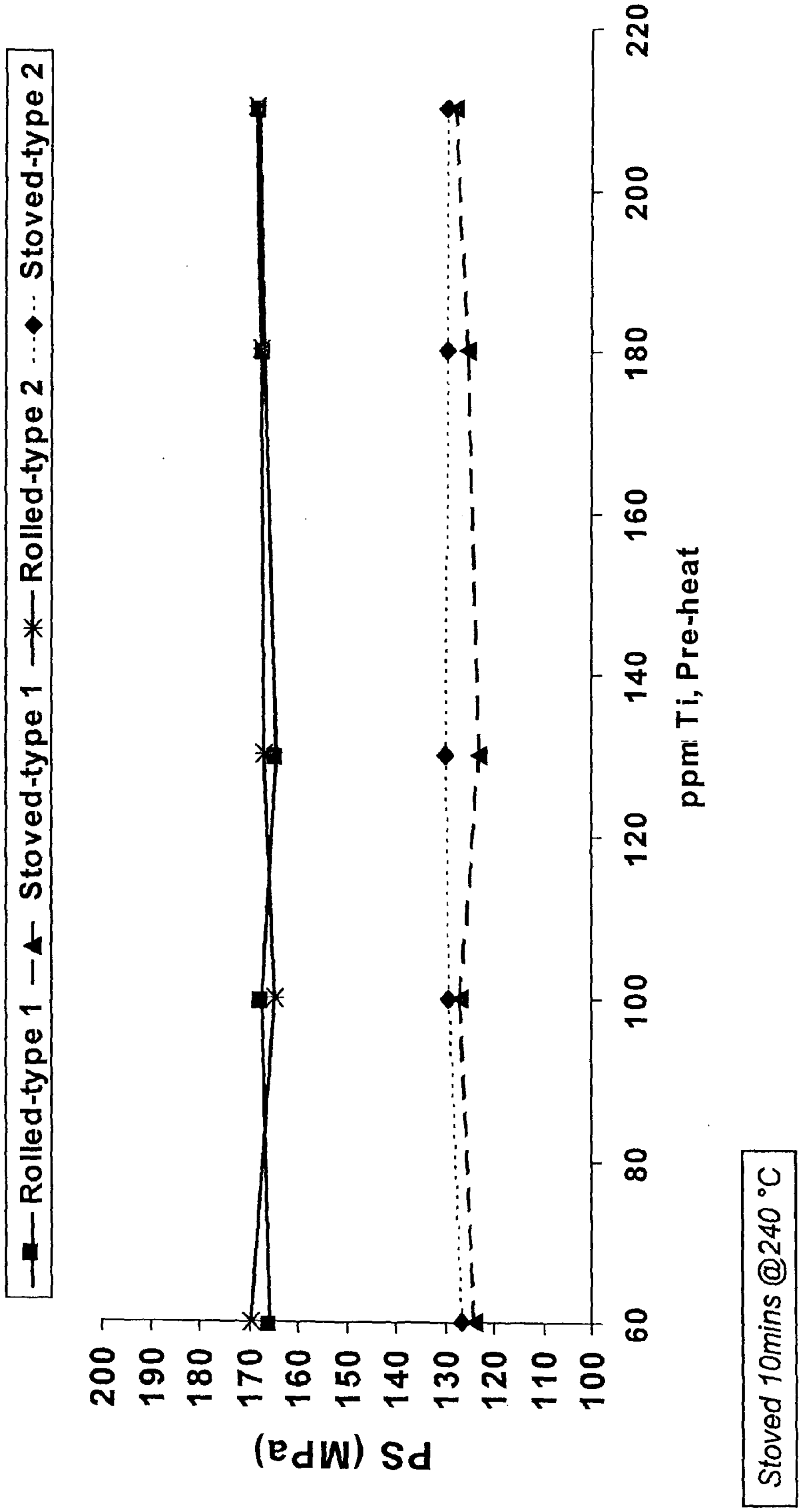

Rolled-type 1
Stoved-type 1
Rolled-type 2
Stoved-type 2
PS (MPa)
200
190
180
170
160
150
140
130
120
110
100
60
80
100
120
140
160
180
200
220
ppm Ti, Pre-heat
Stoved 10mins @240 °C

Figure 5b

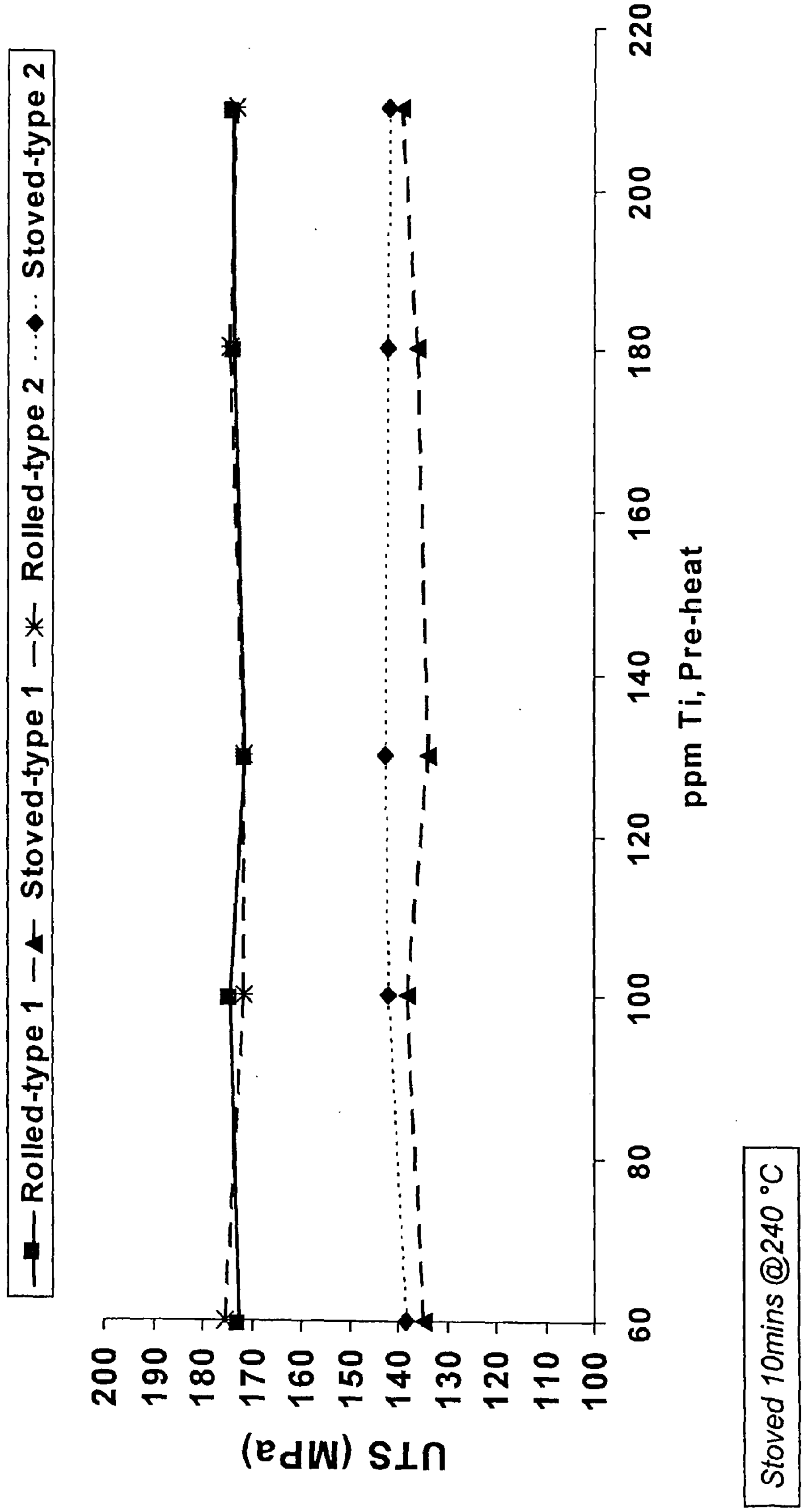

Rolled-type 1
Stoved-type 1
Rolled-type 2
Stoved-type 2
UTS (MPa)
200
190
180
170
160
150
140
130
120
110
100
60
80
100
120
140
160
180
200
220
ppm Ti, Pre-heat
Stoved 10mins @240 °C

Figure 6a

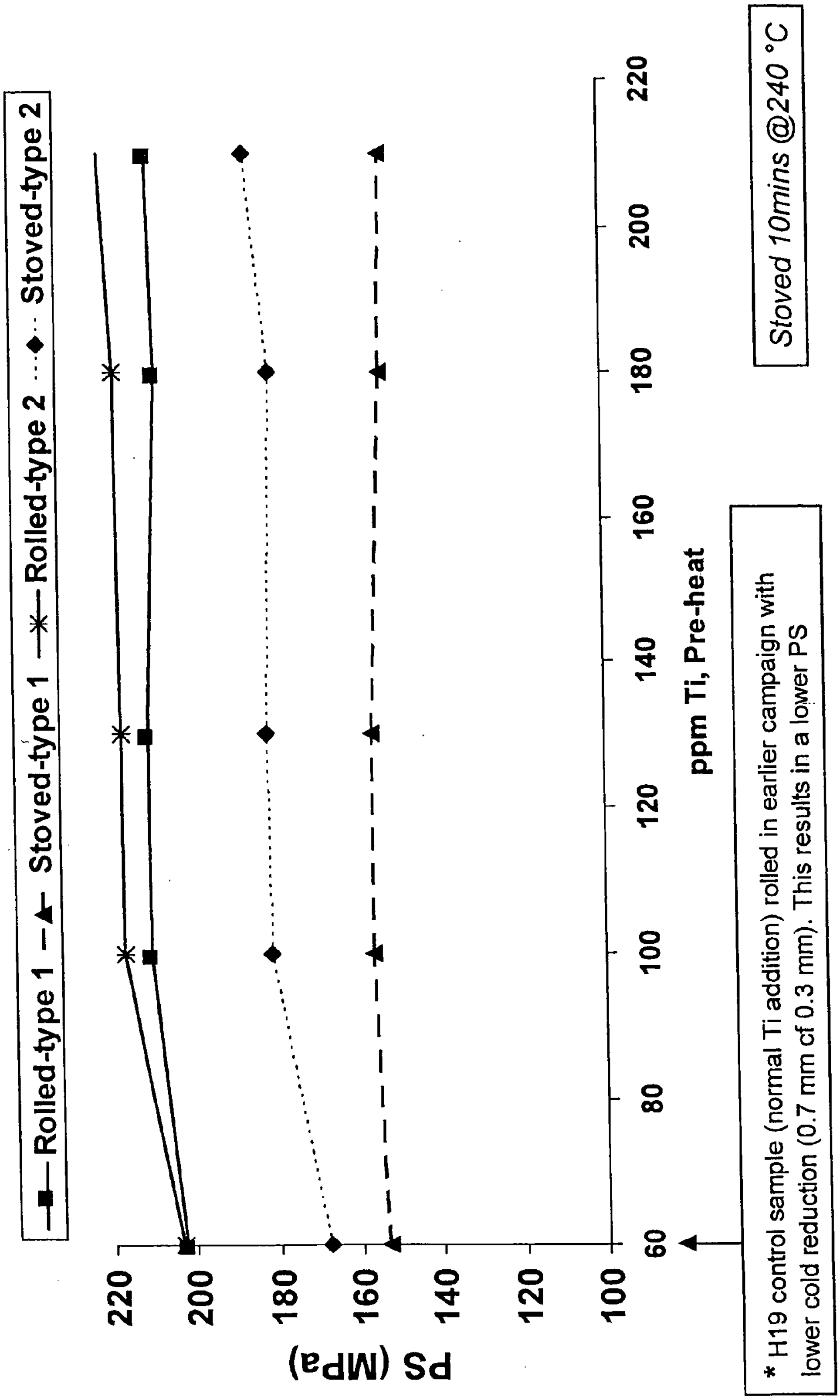

Rolled-type 1
Stoved-type 1
Rolled-type 2
Stoved-type 2
PS (MPa)
220
200
180
160
140
120
100
60
80
100
120
140
160
180
200
220
ppm Ti, Pre-heat
Stoved 10mins @240 °C
* H19 control sample (normal Ti addition) rolled in earlier campaign with lower cold reduction (0.7 mm cf 0.3 mm). This results in a lower PS

Figure 6b

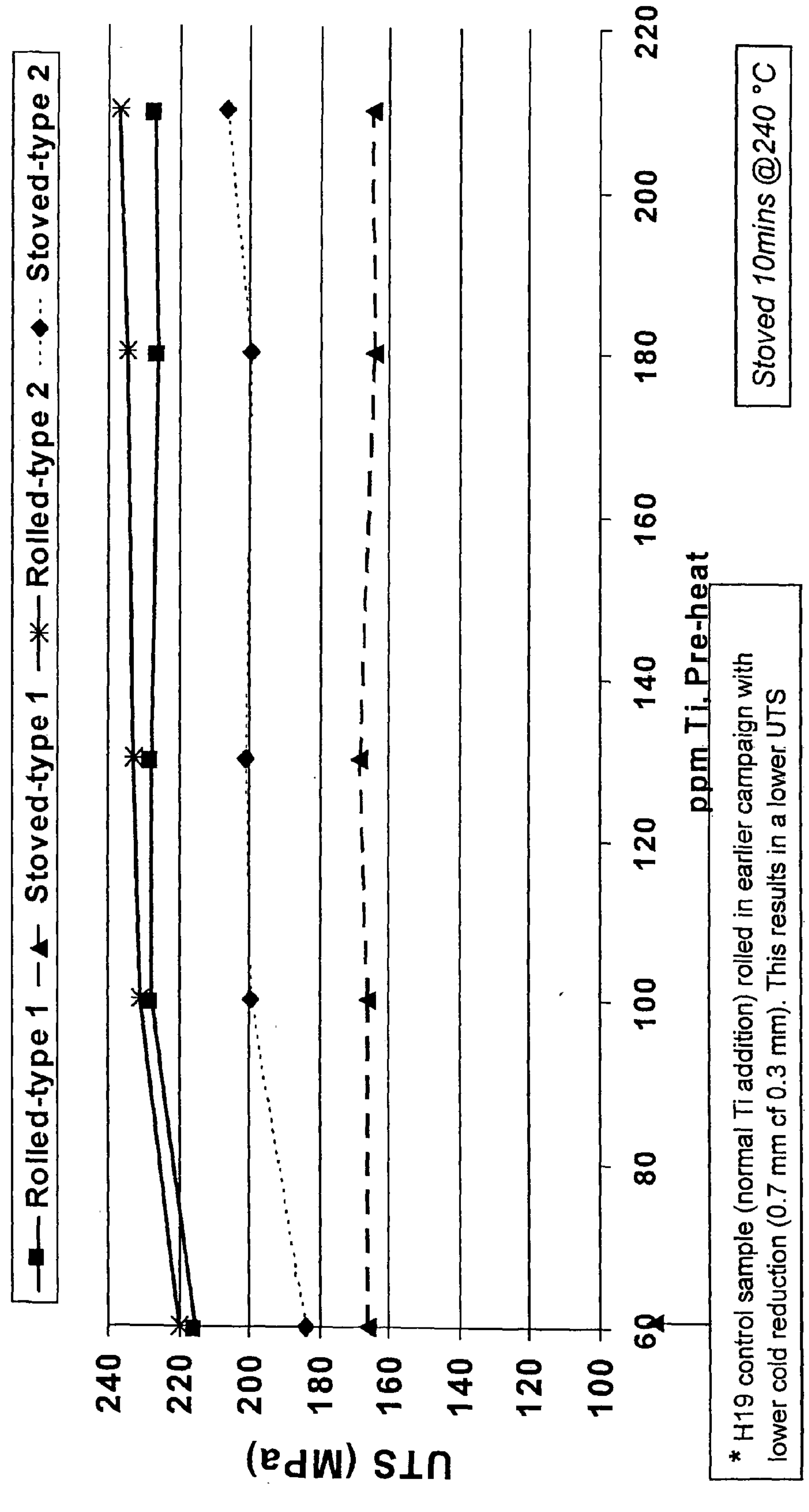
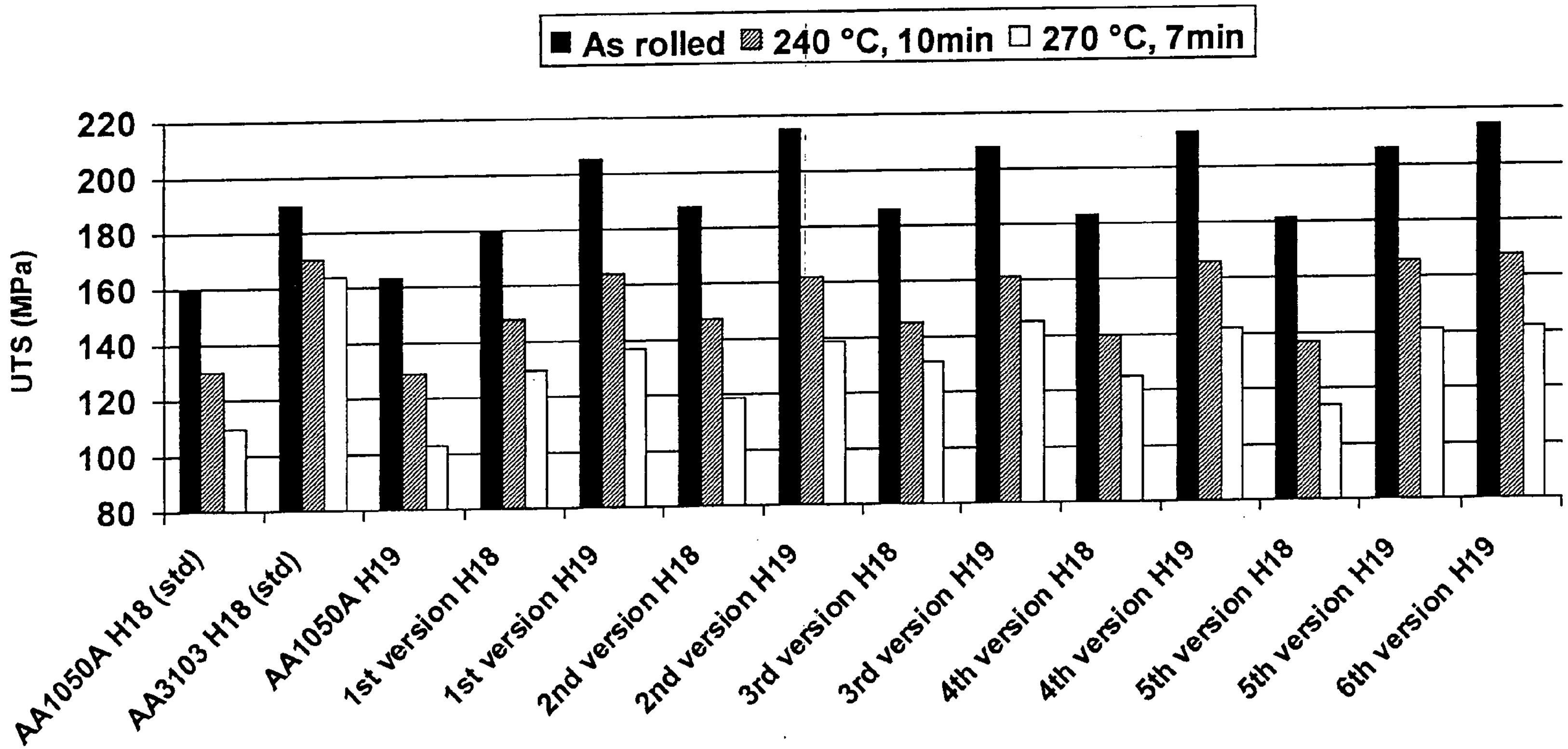
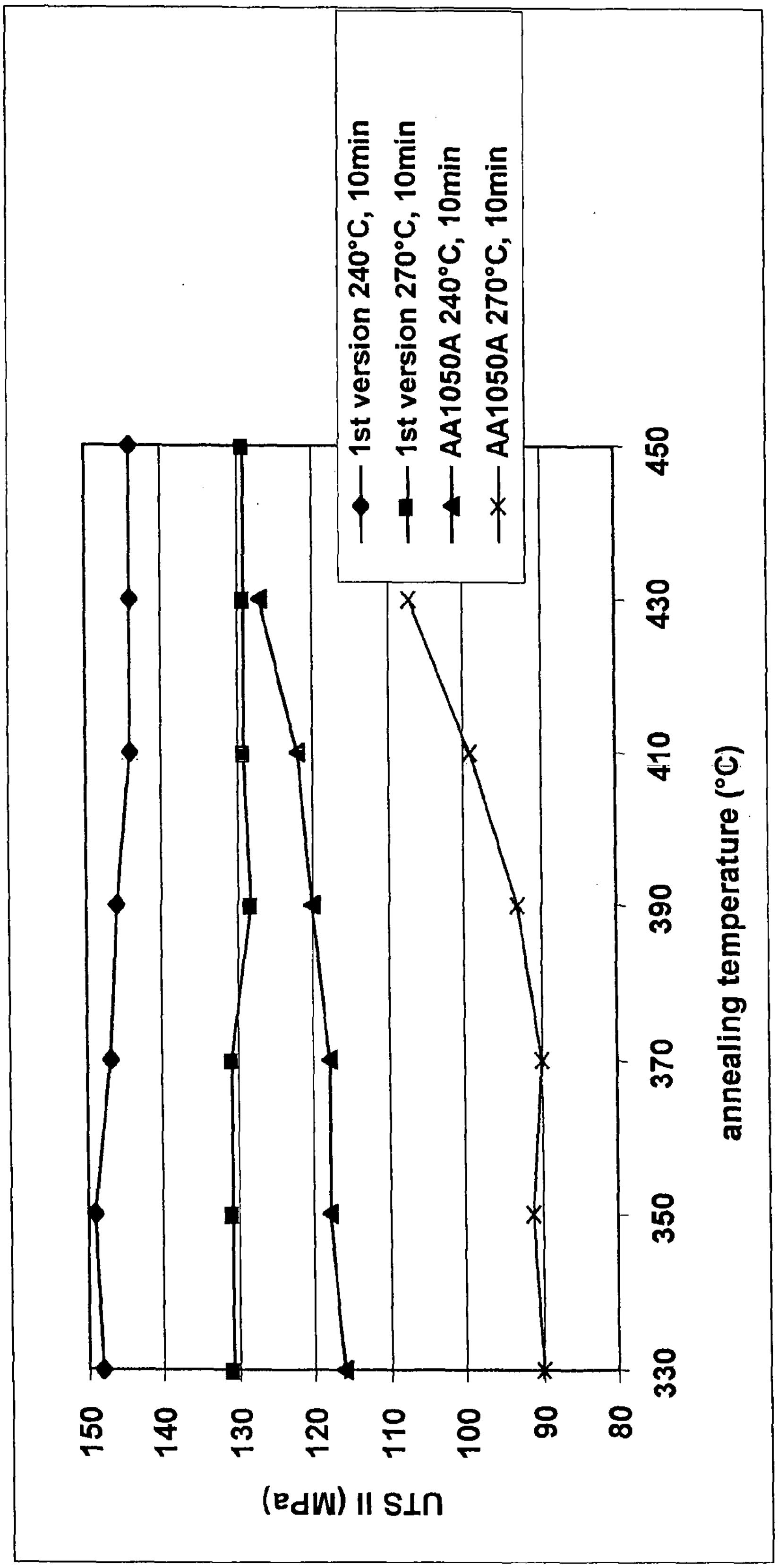

Rolled-type 1
Stoved-type 1
Rolled-type 2
Stoved-type 2
UTS (MPa)
240
220
200
180
160
140
120
100
60
80
100
120
140
160
180
200
220
ppm Ti, Pre-heat
Stoved 10mins @240 °C
* H19 control sample (normal Ti addition) rolled in earlier campaign with lower cold reduction (0.7 mm cf 0.3 mm). This results in a lower UTS

Figure 7. Comparison of mechanical properties (stripes=H19)



Version	Mn(wt%)	Mg (wt%)
1	0.19	0.06
2	0.10	0.13
3	0.06	0.19
4	0.10	0.14
5	0.09	0.08
6	0.10	0.13

Figure 8


1st version 240°C, 10min
1st version 270°C, 10min
AA1050A 240°C, 10min
AA1050A 270°C, 10min
UTS II (MPa)
150
140
130
120
110
100
90
80
330
350
370
390
410
430
450
annealing temperature (°C)

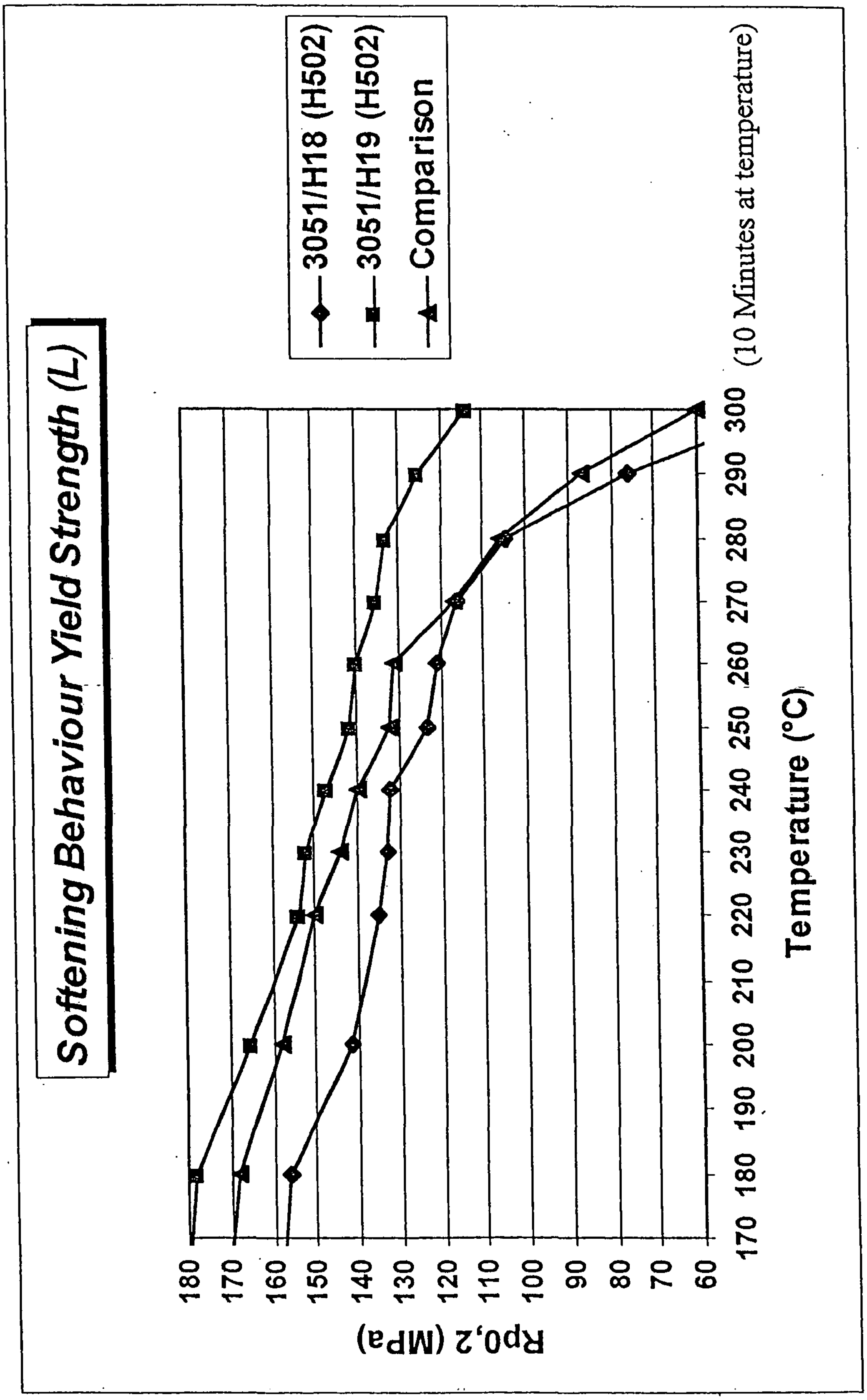

Softening Behaviour Yield Strength (L)
3051/H18 (H502)
3051/H19 (H502)
Comparison
Rp0,2 (MPa)
180
170
160
150
140
130
120
110
100
90
80
70
60
170 180 190 200 210 220 230 240 250 260 270 280 290 300
Temperature (°C)
(10 Minutes at temperature)

FIGURE 9a

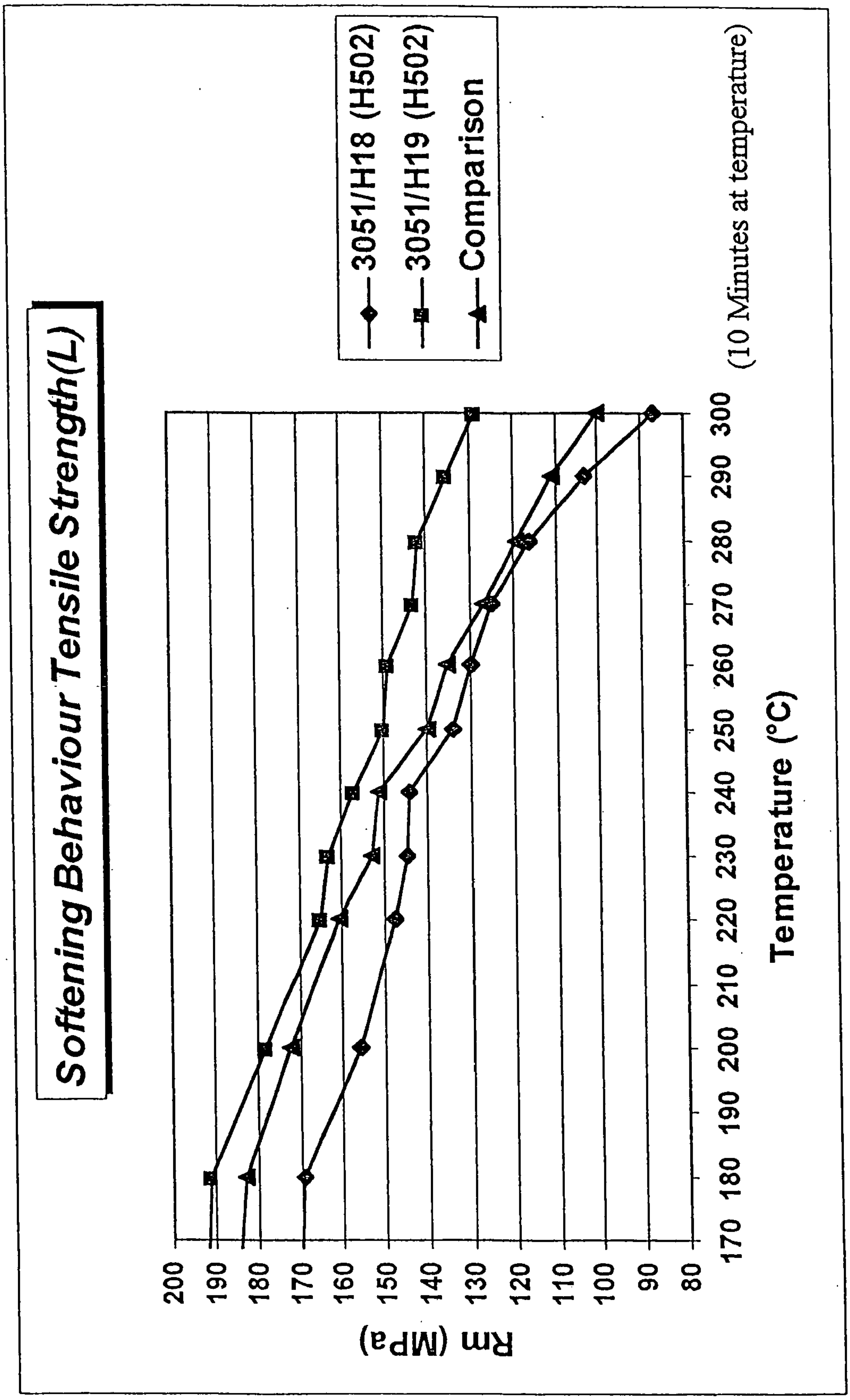
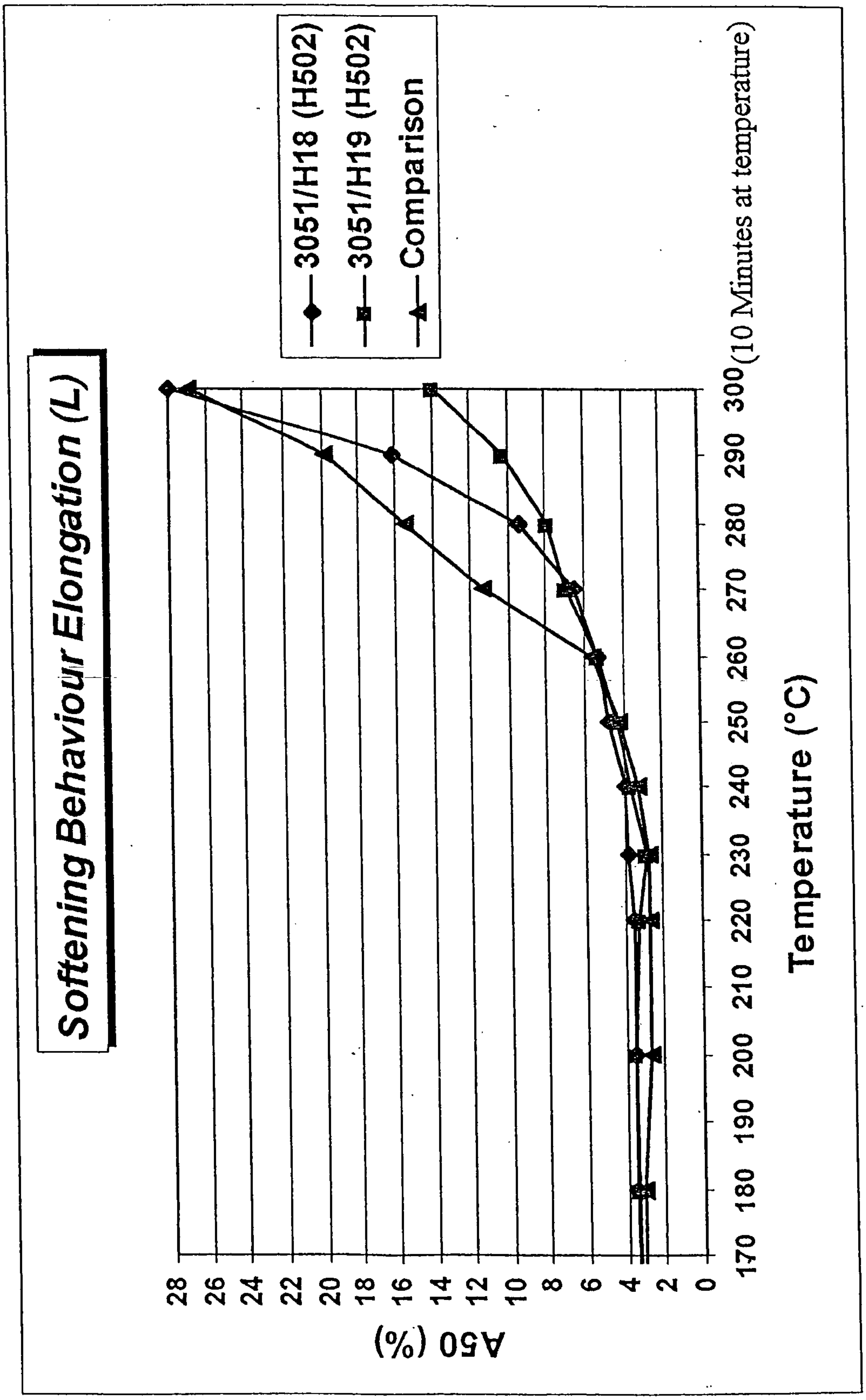

Softening Behaviour Tensile Strength(L)
3051/H18 (H502)
3051/H19 (H502)
Comparison
(10 Minutes at temperature)
Rm (MPa)
200
190
180
170
160
150
140
130
120
110
100
90
80
Temperature (°C)
170
180
190
200
210
220
230
240
250
260
270
280
290
300

FIGURE 9 b



Softening Behaviour Elongation (L)
3051/H18 (H502)
3051/H19 (H502)
Comparison
A50 (%)
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
170
180
190
200
210
220
230
240
250
260
270
280
290
300
(10 Minutes at temperature)
Temperature (°C)

FIGURE 9C