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(71) **Applicant** *(for all designated States except US)*: **UNIVERSITY OF WATERLOO** [CA/CA]; 200 University Avenue W, Waterloo, Ontario N2L 3G1 (CA).

(71) **Applicant and**
(72) **Inventor**: **ESMAEILI, Shahrzad** [CA/CA]; 802-2233 Allison Road, Vancouver, British Columbia V6T 1T7 (CA).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **LLOYD, David, J.** [CA/CA]; 106 Nicholsons Point Road, Bath, Ontario KOH 1G0 (CA). **JIN, Haiou Dr.** [CA/CA]; 1137 Draper Avenue, Kingston, Ontario K7K 7J4 (CA).

(74) **Agents**: **SOJONKY, Andrew, D.** et al.; BORDEN LADNER GERVAIS LLP, World Exchange Plaza, 100 Queen Street, Suite 1100, Ottawa, Ontario K1P 1J9 (CA).

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(54) **Title**: THERMOMECHANICAL PROCESS FOR TREATING ALLOYS

(57) **Abstract**: A thermomechanical process for treating an alloy, for instance an AA6xxx aluminum alloy, to achieve extended high temperature ductility. Such treated alloys may be particularly useful to make automobile panels. First, the alloy is solution heat treated. Next, the alloy is cooled to form a supersaturated solid solution, and is optionally naturally aged. Next, the alloy is plastically deformed to form a high-energy defect structure for subsequent (a) dispersed nucleation of recrystallization, or (b) dispersed recovery-recrystallization, or both (a) and (b), and to form dispersed fine precipitates. Next, the alloy is heated below a recrystallization temperature with a time-temperature profile to continue to form dispersed fine precipitates. Next, the alloy is heated at or above the recrystallization temperature to effect (a) dispersed nucleation of recrystallization and growth of nuclei, or (b) dispersed recovery-recrystallization, or both (a) and (b), to thereby achieve a fine grain structure. The alloy may then be cooled or allowed to cool.

THERMOMECHANICAL PROCESS FOR TREATING ALLOYS

FIELD OF THE INVENTION

[0001] The present invention relates generally to alloys and processing thereof. The invention relates more specifically to a process for thermomechanically treating alloys to achieve a fine grain structure.

BACKGROUND OF THE INVENTION

[0002] Aluminum body panels provide significant weight reductions in automobiles, resulting in fuel efficiency and reduction in greenhouse gas emissions. Al-Mg-Si(-Cu), i.e. AA6xxx, alloys are used for skin (outer) panel applications for their light weight and high strength achieved through precipitation hardening during paint baking processes, as well as good surface appearance. Although these alloys have mainly been used for relatively simple shaped panels (e.g. hoods and trunk lids) and/or in high-end car models, they have not been effectively adopted for the production of more complicated shaped panels (e.g. doors) and/or in the mid-range and economy car classes because of their formability issues and high cost. In comparison with Al-Mg-Si(-Cu) alloys, non-heat treatable Al-Mg, i.e. 5000 series alloys, have overall better formability. However, they are not the alloys of choice for the outer panel applications due to the Ludering problem associated with the magnesium content of the alloys, as well as the lack of hardening potential during paint baking process. Therefore, AA6xxx alloys remain as the most suitable lightweight choice for outer panels. Although the use of 6000 series Al sheets in the automotive industry is continuously growing, the limited formability of the current tempers for shaping complex panels, as well as the inherent springback phenomenon associated with room temperature deformation of aluminium alloys has prevented a stronger growth.

[0003] Reducing the grain size of metals and alloys has been of research interest in the past decade due to the possibility of achieving combinations of desired mechanical properties, unattainable with conventional microstructures [1]. In line with these activities, grain refinement in Al alloys through thermomechanical processing (TMP), and particularly using severe plastic deformation (SPD) processes such as equal channel angular pressing (ECAP), has been pursued [2-5]. These efforts have shown the effectiveness of SPD processes, though in small products, in grain refinement in AA6xxx alloys [e.g. 4-7]. As aluminium alloys with fine-grained microstructures have demonstrated superplastic behaviour at high temperatures (e.g. [8]), manufacturing of fine-grained AA6xxx has the potential to provide an improvement to the formability issue in automotive application of AA6xxx sheets.

[0004] Fine grain AA6xxx alloys have exhibited improved high temperature ductility, and in some cases superplastic behaviour at low strain rates [8-11]. Troeger and co-workers [9-11] have reported that their designed thermomechanical processing route results in superplastic behaviour in their alloy of investigation above 500°C, with optimal superplasticity (strain rate sensitivity of 0.5 and percent elongation 375%) at 540°C at a strain rate of about $5x10\text{-}4s^{-1}$. Similar superplastic behaviour has been reported in warm rolled AA6013 alloy at 560°C and a strain rate of $1x10^{-4}\ s^{-1}$ [12]. Although superplastic forming has been successfully used for forming AA5xxx panels for automotive applications, AA6xxx panels continue to be processed using room temperature stamping operations [4]. The reported strain rate requirement for superplasticity of AA6xxx sheets [9-12] is considered too slow, and therefore inefficient, for automotive panel production. Warm forming is considered as a future solution to the formability limitations of Al sheet for automotive applications and a cost-effective alternative to low volume superplastic processes.

[0005] U.S. Patent No. 6,350,329 (P. Troeger, E.A. Starke, Jr., R. Crooks) [9] describes a fine grain AA6xxx sheet having a composition close to AA6013 and AA6111, with an average grain size of 10 μm and superplastic behaviour, processed using conventional cold rolling and a sequence of heat treatments. It is also indicated that the process is suitable for processing any age-hardenable alloy. The processing, characterization, and properties of the fine grain AA6xxx sheet has also been published as journal papers [10,11]. The heat treatment and cold working steps described in U.S. Patent No. 6,350,329, are as follows:

1. Solution heat treatment followed by rapid cooling to a low temperature (e.g. quenching in medium such as water, oil or air).

2. Sufficient plastic deformation to form a high energy defect structure (e.g. 60% cold rolling)

3. Aging to induce nucleation and growth of precipitates. Multi-step aging, involving low temperature aging followed by high temperature aging (e.g. 24 hours at 300°C followed by 24 hours at 380°C) is preferred. The alloy should be cooled after aging preferably by air cooling.

4. Plastic deformation to induce particle simulated nucleation (PSN) of new grains (e.g. 20% to induce a total of 80% thickness reduction if Step 2 was 60%).

5. Static recrystallization, preferably using a rapid heat up to the recrystallization temperature to minimize the recovery process (e.g. rapid heating to 540°C , followed by 5 minutes at 540°C).

[0006] The above process requires long multi-step procedures (which would also require multiple coiling/uncoiling of the processed sheet during a commercial production), and batch annealing at step 3, which greatly increases the cost of the process.

[0007] The fine grain AA6xxx alloy, produced according the above TMP route results in superplastic behaviour with a maximum strain rate sensitivity of 0.5 and 375% elongation at 540°C for the strain rate range of $2x10^{-4}$ $s^{-1}$to $5x10^{-4}$ s^{-1}. It should be mentioned that this strain rate range is more favourable for high-cost aerospace applications due to slow rate of deformation than for automotive panel forming (see e.g. [2]).

SUMMARY OF THE INVENTION

[0008] It is an object of the present invention to obviate or mitigate at least one disadvantage of previous processes and/or alloys.

[0009] In a first aspect, the present invention provides a process of imparting a fine grain structure to a heat treatable alloy, the process comprising: providing a heat treatable alloy having a precipitating constituent; solution heat treating the alloy; cooling the alloy to form a supersaturated solid solution; plastically deforming the alloy to form a dispersed high-energy defect structure for subsequent (a) dispersed nucleation of recrystallization, or (b) dispersed recovery-recrystallization, or both (a) and (b), and to form dispersed fine precipitates; heating the alloy below a recrystallization temperature with a time-temperature profile to continue to form dispersed fine precipitates; and heating the alloy at or above the recrystallization temperature to effect (a) dispersed nucleation of recrystallization and growth of nuclei, or (b) dispersed recovery-recrystallization, or both (a) and (b), to thereby form a fine grain structure.

[0010] The following embodiments are mentioned. The alloy may be non-isothermally heated to a temperature that is at or above the recrystallization temperature and then may be isothermally heated at the temperature at or above the recrystallization temperature. The heating below the recrystallization temperature and the heating at or above the recrystallization temperature both may consist essentially of non-isothermal heating. The heating below the recrystallization temperature may comprise a mixture of non-isothermal heating and isothermal heating. The heating below the recrystallization temperature may be heating below 300°C. The heating at or above the recrystallization temperature may be heating at or above 300°C. The fine grain structure may be achieved in the absence of further plastic deformation after the heating below the recrystallization temperature. The alloy may be an aluminum alloy. The alloy may be an AA6xxx alloy. The alloy may be an AA6xxx alloy with or without additional incidental or minor alloying elements. The alloy may be a multi- or bi-layered material, wherein at least one layer comprises an AA6xxx alloy and at least one other layer comprises another aluminum alloy. The another aluminum alloy may be an AA1xxx or AA3xxx alloy. The alloy may be an AA6451, AA6111, AA6013, AA6061, AA6063, or AA6066 alloy. The alloy may be an AA6451 or a Cu-free version of AA6451. The alloy may be a heat treatable titanium, magnesium, cobalt, copper, or nickel alloy. The cooling prior to plastically deforming may comprise quenching. The plastically deforming may comprise cold rolling. The plastically deforming may comprise cold rolling the alloy with a reduction of at least 50%. Between the cooling which follows the solution heat treating and the plastically deforming, the process may further comprise naturally aging the alloy. The alloy may be heated continuously to or above the recrystallization temperature. After heating at or above the recrystallization temperature, cooling the alloy or allowing the alloy to cool may be allowed. In one embodiment, the alloy is an AA6451 or a Cu-free version of AA6451; the plastically deforming comprises cold rolling the alloy with a reduction of at least 50%; the alloy may be non-isothermally heated at a rate of less than 40°C/s to a temperature that is at or above the recrystallization temperature and then is isothermally or non-isothermally heated at the temperature at or above the recrystallization temperature; the average grain size of the fine grain structure is less than 25μm; and after heating at or above the recrystallization temperature, the alloy is cooled or allowed to cool.

[0011] In a further aspect, the present invention provides an alloy sheet produced by a process disclosed herein. The alloy sheet may comprise the following properties: a ductility of greater than 80% elongation at 350°C to 550°C and a strain rate of $5x10^{-4}s^{-1}$ to $6.7x10^{-1}s^{-1}$; an average grain size of less than 25μm; and a grain stability, quantified by an increase in average grain size of less than 100% over one hour at 550°C, and an increase in average grain size of less than 10% over one hour at 400°C.

[0012] In a further aspect, the present invention provides an AA6xxx alloy sheet comprising the following properties: a ductility of greater than 80% elongation at 350°C to 550°C and a strain rate of $5x10^{-4}s^{-1}$ to $6.7x10^{-1}s^{-1}$; an average grain size of less than 25μm; and a grain stability, quantified by an increase in average grain size of less than 100% over one hour at 550°C, and an increase in average grain size of less than 10% over one hour at 400°C.

[0013] In a further aspect, the present invention provides an AA6xxx alloy sheet comprising the following properties: a ductility of greater than 80% elongation at 350°C to

550°C and a strain rate of $5x10^{-4}s^{-1}$ to $6.7x10^{-1}s^{-1}$; an average grain size of less than 25μm; and a substantially uniform precipitate distribution below solvus temperature with precipitates substantially in one of more of the following shapes: oval, rounded, and cuboid.

[0014] Other aspects and features of the present invention will become apparent to those ordinarily skilled in the art upon review of the following description of specific embodiments of the invention in conjunction with the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] Embodiments of the present invention will now be described, by way of example only, with reference to the attached Figures, wherein:

Fig. 1 is a schematic of the process described in U.S. Patent No. 6,350,329;

Fig. 2 is a process according to an embodiment disclosed herein (called Route A);

Fig. 3 is a process according to an embodiment disclosed herein (called Route B);

Fig. 4 is a process according to an embodiment disclosed herein (called Route C);

Fig. 5 is a microstructure of an AA6451 sheet processed according to an embodiment disclosed herein (by Route A1);

Fig. 6 is a graph showing the grain size distribution of an AA6451 sheet processed according to an embodiment disclosed herein (Route A1);

Fig. 7 is a microstructure of an AA6451 sheet processed according to an embodiment (Route A1), followed by an extended thermal stabilization;

Fig. 8 is a graph showing the grain size distribution of an AA6451 sheet processed according to an embodiment disclosed herein (Route A1), followed by an extended thermal stabilization;

Fig. 9 is an SEM image (back-scattered mode) from an AA6451 sample continuously annealed (at a heating rate of 0.4°C/min) from 50°C to 360°C and held at 360°C for 6 hours;

[0016] Fig. 10 is an SEM image (secondary electron mode) showing the precipitate structure of a T4P sheet (commercially produced) AA6451 after aging for 2 hours at 350°C;

[0017] Fig. 11 is an SEM image (secondary electron mode) showing the precipitate structure of a T4P sheet (commercially produced) AA6451 after aging for 2 hours at 350°C;

[0018] Fig. 12 is a EDS analyzed image of a commercially produced T4P sheet (AA6451) after aging for 2 hours at 350°C;

[0019] Fig 13 is an image of the fine grain (FG) material heated for 2 hours at 350°C;

[0020] Fig. 14 is an image of a commercial material (T4P) heated for 2 hours at 350°C;

[0021] Fig. 15 is an SEM (secondary electron mode) image showing the precipitate structure of an FG sheet produced by Route A1, after aging for 2 hours at 350°C;

[0022] Fig. 16 is an SEM (secondary electron mode) images showing the precipitate structure of an FG sheet produced by Route A1, after aging for 2 hours at 350°C;

[0023] Fig. 17 is a high magnification view of a commercial material (T4P) after isothermal heating at 450°C for 2 hours;

[0024] Fig. 18 is a high magnification view of a FG material after isothermal heating at 450°C for 2 hours;

[0025] Fig. 19 shows the microstructure of an FG sheet processed through Route A1 (AA6451);

[0026] Fig. 20 shows the microstructure of a commercially produced AA6451 sheet;

[0027] Fig. 21 is a graph showing elongation to failure of a commercial material (T4P);

[0028] Fig. 22 is a graph showing elongation to failure of an FG material

[0029] Fig. 23 is an SEM fracture surface of a commercial (C) sheet;

[0030] Fig. 24 is an SEM fracture surface of an FG sheet;

[0031] Fig. 25 shows grain size evolution of an FG sheet (AA6451-ROUTE A1) after isothermal hearing at various temperatures, measured using EBSD on planar surface cross-section;

[0032] Fig. 26 is a graph showing deformation behaviour of an FG sheet and a C sheet at a strain rate of 5.0×10^{-4} s^{-1};

[0033] Fig. 27 is a graph showing deformation behaviour of an FG sheet and a C sheet at a strain rate of 6.7×10^{-1} s^{-1};

[0034] Fig. 28 is a stress strain curve of a T4P sheet tensile tested at 5.0×10^{-4} s^{-1};

[0035] Fig. 29 is a stress strain curve of an FG sheet tensile tested at $5.0\text{x}10^{-4}$ s^{-1};

[0036] Fig. 30 is a stress strain curve of a T4P sheet tensile tested at $6.7\text{x}10^{-1}$ s^{-1};

[0037] Fig. 31 is a stress strain curve of an FG sheet tensile tested at $6.7\text{x}10^{-1}$ s^{-1};

[0038] Fig 32 is an optical microscopy image (through-thickness cross section) of deformed (i.e. tensile tested) and fractured sample of a C sheet at 350°C and a strain rate of $5.0\text{x}10^{-4}s^{-1}$;

[0039] Fig 33 is an optical microscopy image (through-thickness cross section) of deformed (i.e. tensile tested) and fractured sample of a FG sheet at 350°C and a strain rate of $5.0\text{x}10^{-4}s^{-1}$;

[0040] Fig. 34 is cross-section of a fractured tensile test sample at 500°C and $5.0\text{x}10^{-4}$ s^{-1} of a C sheet; and

[0041] Fig. 35 is a cross-section of a fractured tensile test sample at 500°C and $5.0\text{x}10^{-4}$ s^{-1} of an FG sheet.

DETAILED DESCRIPTION

[0042] Generally, according to one embodiment, there is disclosed a thermomechanical process for treating an alloy, for instance an AA6xxx aluminum alloy, to achieve extended high temperature ductility. Such treated alloys may be particularly useful to make automobile panels. First, the alloy is solution heat treated. Next, the alloy is cooled to form a supersaturated solid solution, and is optionally naturally aged. Next, the alloy is plastically deformed to form a high-energy defect structure for subsequent (a) dispersed nucleation of recrystallization, or (b) dispersed recovery-recrystallization, or both (a) and (b), and to form fine precipitates. Next, the alloy is heated below a recrystallization temperature with a time-temperature profile to continue to form dispersed fine precipitates. Next, the alloy is heated at or above the recrystallization temperature to effect (a) dispersed nucleation of recrystallization and growth of nuclei, or (b) dispersed recovery-recrystallization, or both (a) and (b), to thereby form a fine grain structure. The alloy may then be cooled or allowed to cool.

[0043] Without intending to be bound by theory, the present process involves forming dispersed precipitates during early stage (i.e. low temperature) annealing. These finely distributed precipitates grow during further annealing (at higher temperature) such that they interact with recovery and recrystallization mechanisms and induce the formation of dispersed new grains. The precipitates later interact with grain boundary movement inhibiting rapid grain growth during extended exposure to high temperatures.

[0044] An embodiment of the thermomechanical processing (TMP) can be summarized as follows (Figs. 2 to 4 illustrate three of many possible routes of this process):

[0045] 1. Solution heat treatment of a heat treatable alloy having a precipitating constituent, followed by rapid cooling to a low temperature (e.g. quenching in medium such as water, oil, or air). The minimum temperature is the solvus temperature and the maximum temperature is the solidus temperature (these terms refer to temperature-concentration boundaries in an alloy phase diagram). Rapid cooling may be air cooling (which is relatively slow), water quenching (which is faster), an even faster method such as cooling in a salt water solution, or another known method. There is no specific maximum cooling rate.

[0046] 2. Optional storage at about room temperature (i.e. during which time natural aging can occur, which can be beneficial) for a time such as one day, one week, two weeks, or four weeks, which allows for the process to be integrated with existing infrastructure and operations) followed by sufficient plastic deformation (e.g. at least 30%, or at least 50%, or 60 to 80% reduction, dependent on the alloy type, by conventional or asymmetric cold rolling). This induces a high energy defect structure (large dislocation density), with a fine distribution of small solute clusters depending on the storage time at about room temperature. The minimum thickness reduction will depend on the alloy. There is no specific maximum thickness reduction. The preferred reduction amount, based on current commercial line capabilities for the initial thickness and common aluminum sheet thickness for automotive panels, for AA6xxx alloys, is about 60 to 70%; for instance beginning with a 2.5mm sheet and finishing with a 1mm sheet, or beginning with a 5mm plate and finishing a 1.5mm sheet. These thicknesses are mere examples. Various starting and finishing thicknesses may be selected, and may be based on, for instance, the alloy, the desired product specification, or line requirements.

[0047] 3. Annealing through heating of the as-deformed material from a low temperature (e.g., room temperature, 50°, 100°C, less than 300°C, or less than the recrystallization temperature of the alloy) to a high enough temperature (e.g. 300°C and above, or at least to the recrystallization temperature of the alloy) to induce recrystallization (e.g. substantial or full recrystallization) and a fine grain structure. The lowest preferred starting temperature may depend on the capability of the infrastructure/production line or the preferred operating conditions, as well as the alloy type. The maximum starting temperature may be between 250 to 350°C for AA6xxx alloys, corresponding to the approximate temperature range for the "nose" (also known as "knee") of the TTT (time-temperature-transformation) diagram for these alloys [13]. The starting temperature lower than the nose of the TTT diagram will increase the number density of precipitates within the grains and decrease the possibility of grain boundary precipitation due to a high driving force for homogeneous nucleation of precipitates and/or precipitation on dislocations accumulated during deformation. A high number density of precipitates within the grains and prevention of any major grain boundary precipitation are factors in creating the desirable sheet structure. It is noted that the general term "precipitates" may include all precipitate forms such as solute clusters, GP zones, metastable precipitates, transitional precipitates, and equilibrium precipitates. The finishing temperature is a temperature at which a substantial fraction of grains recrystallize (e.g. fraction recrystallized: 90%, 95% or 99%) at the selected production time. A shorter required time usually requires a higher temperature, as recrystallization is a thermally-activated process and therefore dependent on time at temperature. A higher % reduction in the thickness during the deformation stage can also significantly affect the maximum temperature achieved. A higher percent reduction in the thickness usually requires lower temperature and/or shorter times to achieve substantial recrystallization. The preferred maximum temperature is ≥ 300°C in AA6xxx alloys. Preferably, the maximum limiting temperature is the practical solidus temperature (i.e. melting should not happen).

[0048] "Recovery-recystallization" is used herein to include less than full continuous recovery-recrystallization. This mechanism may occur over a substantial, but not necessarily the entire, portion of the bulk material. For instance, there may be sporadic nucleation of recrystallization in some locations of the material as well, but the main mechanism which occurs is the continuous one.

[0049] The preferred annealing process is ramp heating from the selected low temperature with a selected heating rate (e.g. 0.4°C/min). This is preferred to make use of the existing aluminum rolled product production lines with minimal requirement for change in the production line and no wait time or batch annealing process. There is no specific minimum heating rate and the maximum will depend on the particular alloy used and whether the ramp heating is combined with any other heating and/or cooling step (e.g. isothermal step or another non-isothermal heating, or a cooling step). When there is no additional step (i.e. Route A and B), the maximum ramp heating rate is also dependent on the choice of the maximum temperature; a lower maximum rate is needed when the highest temperature is relatively high (e.g. 0.4°C /min to reach 380°C and no isothermal time at this temperature, or 100°C/min to reach 310°C and 24 hours at this temperature). If, after the initial ramp heating, there is at least one additional step which provides some time below the nose of the TTT diagram, the ramp heating can be as fast as possible. (As an example for AA6xxx alloys, extremely fast heating from room temperature to 100°C, 2 hours at 100°C, 4°C /min to 360°C, 1 hour at 360°C.). The key requirement is to allow sufficient time below the nose of the TTT diagram to form a high number density of fine precipitates and then allow enough time at a relatively high temperature to achieve the recrystallization requirement. The large number density of fine precipitates either prevents recovery and the rapid formation of dislocation cell structures or it promotes a continuous recovery-recrystallization process. In the former case, the inhibition of recovery preserves a large driving force for the nucleation of new deformation-free grains (i.e. nucleation of recrystallization) at all, or most, high energy sites (e.g. abundant dislocation bundles, shear bands, around large pre-existing intermetallic particles) and therefore results in a fine grain microstructure. These mechanisms do not require the particle-simulated nucleation (PSN) mechanism for grain refinement, as used by U.S. Patent No. 6,350,329, mentioned above.

[0050] U.S. Patent No. 6,350,329 uses, after solution the heat treating, the plastic deformation, and the annealing, another plastic deformation and subsequent static recrystallization. In U.S. Patent No. 6,350,329, a second deformation is required. In the instant case, a second deformation is not required as the first deformation is sufficient to produce the defect structure required by the subsequent step. In U.S. Patent No. 6,350,329, an aging step is required to start the precipitation process and make the precipitates large enough so that they act as the sites to accumulate strain energy during the second round of deformation. Then, those high energy sites will act as nucleation sites for the new (i.e. recrystallized) grains during the annealing stage at the higher temperature. Therefore, the mechanism of recrystallization is particle simulated nucleation of new grains (i.e. PSN). In the present case by contrast, strain energy is accumulated in a dispersed fashion ("dispersed" means substantially uniformly across the bulk material but may include areas that are non-uniform such as due to the presence of large pre-existing particles and grain boundaries which accumulate larger levels of strain energy). Simultaneous with this deformation, fine precipitates form (such as nano-size). They continue to form during the early stage of annealing (called nucleation and growth of precipitates). The nuclei can be in the form of atom clusters or well developed zones, precipitates, etc. Some time at relatively low temperatures allow the disperse formation of these precipitates. The precipitate nucleation and growth is usually enhanced due to the defect structure (high energy state promotes nucleation and the defects promote diffusion (i.e. movement) of solute atoms which attach themselves to the nucleated precipitates and cause their growth to be faster). These finely distributed precipitates then pin the dislocation motion so that their recovery (i.e. elimination) does not happen quickly and they remain as high energy sites. Then, two mechanisms are possible: (a) when high energy sites are maintained, new grain nucleate (recovery and recrystallization in this case are competitive processes and less recovery means more chance for new grain nucleation). This process results in numerous new grains and therefore a fine grain structure; and (b) another mechanism (process) that may happen is that the precipitates pin the dislocations so that fast recovery does not, or does not substantially, happen. However, a recovery-recrystallization process happens (no new nuclei, or substantially no new nuclei, form) but the dislocation structure renders itself gradually to a new dislocation arrangement that gradually changes to new grains everywhere. This is called recovery-recrystallization process or a continuous recovery-recrystallization process. The study on AA6451 following Route A, suggests that option (a) happens in that case. However, changing the route and the temperature and temperature rate choices can result in mechanism (b). Grain refinement here does not depend, or depend substantially, on PSN. In the present case, precipitates are not intended for the accumulation of high strain energy to act as nucleation sites for recrystallization. They are rather used to pin the dislocation movement and later to pin the grain boundaries of the new grains so that the grains do not grow to large sizes (i.e. helping with grain size stability). Certain factors in achieving a stable grain size are (1) a large number of dispersed new grain nucleation (due to the pinning effect precipitates exert on dislocations) and (2) pinning of the boundaries of these grains by the dislocations. If the number of nuclei were small or they were not dispersed, a wide grain size distribution would occur and would encourage grain growth and coarsening (i.e. large grains grow larger at the expense of the smaller grains). Some grain growth is inherent in extended annealing processes.

[0051] Routes A and B (Figs. 1 and 2, respectively) show preferred annealing routes for their enhanced compatibility with current commercial sheet production lines. It is noted that only one stage of deformation is present (e.g. rolling).

[0052] Route C (Fig. 3) shows annealing where the heating is not solely non-isothermal. That is, there may be one or more steps of isothermal heating.

[0053] Alternative routes may be used in accordance with the production line requirements or preferred operations or final product properties (e.g. fraction recrystallized, level of strength, ductility or potential for better corrosion resistance). These routes can have multiple isothermal and non-isothermal steps including heating and cooling cycles, heating with non-linear rates, and non-linear rate heating and cooling cycles.

[0054] The process may provide a cost-effective and efficient process of sheet production with the use of existing production facilities and minimal need for change in the production lines.

[0055] As compared to commercially processed AA6xxx sheets, which are available to the automotive industry at present, the produced sheets of embodiments of the instant invention may be a better choice for the automotive industry to achieve cost-effective forming of complex shape panels, which require high levels of ductility. Of course, the resultant alloy sheets could be used in various applications where one or more properties of these resultant alloy sheets, for instance the fine grain size and good ductility, could be exploited.

[0056] The Alloy

[0057] Heat treatable alloys, such as a 2xxx, 6xxx, 7xxx and some 8xxx aluminum alloys having a precipitating constituent, are conceivably candidates for processing in accordance with embodiments of this invention. In order for an alloy to be heat treatable, it should have at least one alloying element that is different from the element of the matrix, (e.g. Al-Cu alloys with Al acting as the matrix and Cu acting as the precipitating constituent forming a series of Cu-Al containing precipitate phases). The precipitates are used during annealing to help create and retain a fine grain structure by affecting recovery, recrystallization, and grain growth processes. The fine distribution and morphology of these precipitates, achieved through the instant process, also significantly contribute to the desirable ductility of the fine grain (FG) materials (e.g. in contrast to the precipitate morphology and distribution in the current commercially processed AA6xxx materials.).

[0058] Solution Heat-Treating

[0059] The alloy selected for processing is solution heat-treated in the conventional manner. It will be readily appreciated that the temperature and heating time of this step depend upon the type and thickness of the alloy being processed. In any event, the alloy should be heated to a temperature below that at which melting begins, and the heating time should be sufficient to achieve the dissolution of normally soluble phases.

[0060] Rapid Cooling

[0061] Following solution heat-treatment, the alloy is cooled to form a supersaturated solid solution. Although the mode of cooling is not critical, rapidly cooling the alloy to a temperature at which the diffusion rate of any of the elements in the alloy is not appreciable, and the formation of precipitates, particularly on the grain boundaries, is practically prevented, ensures the retention of as much solute in solid solution as possible, making the maximum amount of solute available for the subsequent formation of finely distributed precipitates during early stage annealing. Some precipitation, such as solute cluster formation, may occur during rapid cooling, and is acceptable. Prevention of major precipitate formation also ensures low strength and therefore ease of deformation during the plastic deformation step. The rapid cooling may be accomplished, for example, by quenching in a medium such as water, oil or air, or another known rapid cooling mechanism.

[0062] Plastic Deformation

[0063] Once solution heat-treatment is complete, the alloy is sufficiently plastically deformed to produce a high-energy defect structure useful for subsequent (a) dispersed nucleation of recrystallization and growth of nuclei, or (b) dispersed recovery-recrystallization, or both (a) and (b).

[0064] Many processes for plastically deforming a material are known to those skilled in the art, such as rolling, stretching, extrusion, pressing, drawing, forging, torsion processes, and a combination of these processes, among others. It is anticipated that any mode of plastic deformation may be used, so long as it is sufficiently severe to produce the required high-energy defect structure in the grains of the material. Preferably, the amount of reduction per pass and number of passes is such that the deformation fully penetrates, or substantially penetrates, the alloy. It is also preferable that the deformation be uniform, or substantially uniform, throughout the thickness of the alloy.

[0065] The deformation of the solution heat-treated alloy is preferably carried out at room temperature, although this temperature will vary with alloy composition. This step also may be carried out at other temperatures. Most preferably, the deformation is performed at whatever temperature is most convenient and economical, provided that sufficient energy is retained in the alloy for the formation of a high-energy defect structure. One example is that magnesium alloys might be deformed at a higher temperature to facilitate extensive reduction in thickness, not achievable at room temperature due to the hcp structure of magnesium.

[0066] It is well-known that some alloying elements enhance the work hardening behavior of alloys when such alloying elements are present in solid solution. For example, magnesium is known to have this effect in aluminum alloys.

[0067] Indeed, aluminum alloys containing Mg in solid solution, may develop greater stored strain energy for a given amount of deformation than alloys not containing Mg (some alloying additions, such as Mg in solid solution in Al matrix are known to lower the dynamic recovery rate). Accordingly, the high-energy defect structure required for such alloys may be more readily attainable for alloys containing one or more alloying elements in solution than for alloys not having such alloying elements. The potential solute cluster formation during rapid cooling or optional storage can also retain or enhance the work hardening behavior of the solid solution alloy, and thus the level of energy storage during deformation, in some alloys such as AA6xxx alloys. These clusters can act as further heterogeneous nucleation sites (or practically as nuclei) for precipitate formation during annealing.

[0068] Some alloys, including AA6xxx alloys, tend to form precipitates during room temperature (or a low temperature) deformation. This type of precipitation has been frequently called a “dynamic precipitation process”. The precipitates that form during deformation later can act as nucleation sites and/or nuclei for further precipitation during early stage annealing.

[0069] Annealing

[0070] Once the alloy has been plastically deformed, it is heated to form fine substantially homogenous distribution of precipitates during early stage (i.e. low temperature) annealing. Again, this is referred to herein as dispersed fine precipitates and may include some areas of heterogeneity. The preferred times and temperatures for the heating process are dependent upon the type of alloy used. These finely distributed precipitates grow and/or coarsen during further annealing (at higher temperature) such that they interact with recovery and recrystallization mechanisms and induce the formation of equi-axed, or relatively equi-axed, new grains with a fine average grain size and a relatively narrow size distribution. The precipitates can (or tend to) later inhibit grain growth during extended exposure to high temperatures. Having a relatively narrow grain size distribution is one reason that the grain size is relatively stable (which can be in contrast to some commercially processed materials). When the grain size distribution is wide, the larger grains tend to grow at the expense of the smaller ones. This provides significant grain growth, which is not the case with the FG material discussed herein.

[0071] The cooling rate after annealing is not critical if the final annealing temperature is below the solvus temperature. If it is above the solvus temperature, a relatively fast cooling rate (e.g. air cooling or cooling with/in a liquid medium at a relatively low temperature such as water at room temperature) is preferred to retain the solutes in the solid solution matrix and mitigate grain boundary precipitation.

[0072] In commercial alloys, large particles might form during casting, solidification, homogenization and hot working processes. These particles do not dissolve during solution heat treatment. These particles may play a role in recrystallization due to their potential PSN effect (i.e. they gather large stored energy during deformation which can later act as nucleation sites for new grains). The level of their contribution to recrystallization depends on their population in the alloy. In AA6451, when the instant TMP was applied, TEM experiments show some new grain nucleation around these particles. However, this effect is minor compared to the main mechanisms described herein. If there is an alloy with much larger population of these pre-existing large particles (in micron size), their contribution to the overall recrystallization will also increase.

[0073] Certain characteristics of the FG sheets produced in accordance with disclosed embodiments will now be described.

[0074] Microstructure

[0075] A fine grain sheet with a relatively equi-axed grain structure was obtained by a process according to a disclosed embodiment, using continuous annealing including non-isothermal heating from 50°C to 380°C for 13 hours and isothermal stabilization at 380°C for 20 minutes (called hereafter Route A1 as it falls within Route A of Fig. 1), applied on AA6451. The microstructure of this sheet and the grain size distribution are shown in Figs. 5 and 6, respectively. The average grain size of the sheet (through thickness) is approximately 8.0 μm (approximately 10 to 11 microns in sheet plane). The microstructure has excellent stability at high temperature. This is evidenced by examining the microstructure of the alloy when the stabilizing step at 380°C is extended to 5 hours. The result is shown in Figs. 7 and 8. The microstructure has barely changed when the alloy is exposed to a temperature of 380°C for an extended period of time.

[0076] Fig. 25 shows grain size evolution of the FG sheet (AA6451-ROUTE A1) after isothermal heating at various temperatures, measured using EBSD on planar surface cross-section. Grain size stability is observed.

[0077] The significance of the relatively stable microstructure is that the grains will resist growing during high temperature deformation and therefore will remain fine for relatively long times at high temperatures. This will result in extended ductility (formability) at high temperatures. If the grains would tend to grow quickly, the microstructure would not remain fine-grained during high temperature deformation. It would then render the material coarse-grained one, similar in grain size and/or size distribution to the existing commercial sheets, with potentially inferior ductility at high temperatures and potentially prone to premature failure during high temperature deformation. Even if the grains grow and make the material coarse-grained, the precipitate morphology (more rounded) and distribution (substantially uniformly distributed everywhere) will make the sheet more ductile compared to the current commercial coarse-grained sheet. Further, the sheet will also still be less prone to premature failure compared to the commercial sheet because of the precipitate structure difference.

[0078] Another characteristic of the microstructure is the precipitate distribution. The annealing process creates dispersed fine precipitates throughout the microstructure. "Dispersed fine precipitates" means substantially uniformly distributed precipitates where major precipitate networks are generally not formed and grown on grain boundaries. Further extended exposure of this microstructure to high temperatures does not change, or substantially change, this characteristic. Fig. 9 shows an SEM image (back-scattered mode) from an AA6451 sample continuously annealed (at a heating rate of 0.4°C/min) from 50°C to 360°C for 6 hours. Precipitates are observed as black particles when back scattered electrons are used to obtain the SEM image. The precipitate distribution is very different in the microstructure of the commercially-produced sheets when exposed to high temperatures, particularly for an extended period of time.

[0079] Figs. 10 and 11 are SEM images (secondary electron mode) showing the precipitate structure of a T4P sheet (commercially produced) AA6451 after aging for 2 hours at 350°C. A network of grain boundary precipitates and fine distribution of small, elongated particles are seen within the grains.

[0080] Fig. 12 is an EDS analyzed image of a commercially produced T4P sheet (AA6451) after aging for 2 hours at 350°C.

[0081] Figs. 13 (FG sheet) and 14 (T4P) at 350°C show that for the T4P material, grain boundary precipitates can be both small and round and elongated.

[0082] Figs. 15 and 16 are SEM (secondary electron mode) images showing the precipitate structure of an FG sheet produced by Route A1, after aging for 2 hours at 350°C.

[0083] Fig. 17 is a high magnification view of the T4P material after isothermal heating at 450°C for 2 hours.

[0084] Fig. 18 is a high magnification view of the FG material after isothermal heating at 450°C for 2 hours.

[0085] Figs. 10 to 18 demonstrate the effect of high temperature exposure to precipitate distribution in the microstructure of a commercially-produced AA6451 sheet. Precipitates are white and light gray particles within the grains and along the grain boundaries (white and light grey network). As seen in Figures 10 and 11, after aging for 2 hours at 350°C, large, blocky and elongated precipitates grow on the grain boundaries, which were not seen in the as-received material. The interior of the grains can be seen to contain smaller, more homogeneously distributed thin elongated precipitates (see Fig. 12). The precipitates at grain boundaries and in grain interiors grow preferentially in certain directions (see Fig. 17), however this relationship is not as clearly seen at lower temperatures, as the grain boundary precipitates appear more oblong in shape. The EDS spectrums in Fig. 12 show that the large blocky particles within the grains contain silicon and oxygen, while the large particles on the grain boundaries contain silicon, copper, and oxygen. The oxygen content is due to the electropolishing procedure, and the removal of the magnesium during electropolishing. Areas immediately around the grain boundaries and grain boundary precipitates have fewer of the smaller precipitates (see Fig. 12).

[0086] The T4P sheet shows precipitates both inside the grains (finely distributed) and along grain boundaries, which form a pronounced network of precipitates; and areas adjacent to the grain boundaries do not have the finely distributed precipitates, as within the interior of the grains. These areas, which are defined as precipitate free zones (PFZ), are weak and prone to premature failure during deformation. The precipitate network itself is also considered deleterious to the properties and/or the performance of the alloys, because of effects such as inducing brittle fracture along the grain boundaries, or stress concentration effects due to the closely spaced elongated precipitates. The precipitate network also creates corrosion problems. The elongated morphology of precipitates that forms during high temperature exposure in the commercially-processed material results in elevated internal stresses and extensive cavitation, and hence low ductility, during high temperature deformation. The FG material does not have the elongated precipitates; rather the precipitates are rounded and finely/homogenously distributed throughout the sheet structure.

[0087] The sheet processed using Route A1 is not prone (or not as prone) to the above undesirable properties. Figs. 19 and 20 provide another direct comparison of the microstructure of the fine-grained sheet produced through Route A1 when exposed to a high temperature with that of the commercial sheet exposed to the same heating condition. The difference in the distribution of precipitates in the two sheets is noticeable. The sheet of Figs. 19 and 20 are AA6xxx alloy sheets (thermomechanically processed and then heated for 15 minutes at 450°C. Figure 19 is a fine grained sheet processed through Route A1 (AA6451) and Figure 20 is a commercially produced AA6451 sheet.

[0088] Mechanical behaviour

[0089] High temperature tensile testing has been performed on the FG sheet (AA6451) fabricated through Route A1, as well as on the commercially produced AA6451 sheet (C sheet, which is in T4P temper condition) at various temperatures in the range of 350°C to 550°C and strain rates in the range of $5.0\text{x}10^{-4}$ $\text{s}^{-1}$to $6.7\text{x}10^{-1}$ s^{-1}. The elongation to failure of the T4P material in each condition is summarized in Fig. 21. The results show that at lower temperatures, 350°C and 400°C, the strain rate has little effect on the elongation to failure. Samples fail at approximately 35% and 50%, respectively, regardless of the strain rate. At 450°C, however, the material begins to be affected by the strain rate. At this temperature, the lowest average strain rate achieves an elongation of approximately 90%, while at the highest strain rate, the average elongation is approximately 125%. At the two highest temperatures, the strain rate has an even more pronounced effect. An increase of almost 100% total elongation to failure going from the lowest to the highest strain rate was found. The maximum average elongation to failure was seen at 550°C at a strain rate of $6.7\mathrm{x}10^{-1}\mathrm{s}^{-1}$ with approximately 225%.

[0090] Fig. 22 summarizes the total percent elongation to failure of the FG material at each temperature and strain rate. At 350°C and 400°C, increased strain rate does not lead to an appreciable change in the total elongation. The average elongations seen at these temperatures are in the approximate range of 110 to 135%. At the three highest temperatures, the FG material trends towards increasing elongation with increasing strain rate up to intermediate strain rates (i.e. $1.0\mathrm{x}10^{-2}\ \mathrm{s}^{-1}$ for 450°C and $2.0\mathrm{x}10^{-2}\ \mathrm{s}^{-1}$ for 500 and 550°C), beyond which the elongation to failure does not further increase. The maximum average elongation to failure seen in this material is approximately 220% at 550°C and a strain rate of $2.0\mathrm{x}10^{-2}\mathrm{s}^{-1}$.

[0091] It should be noted that the % elongation values reported here for high temperature (i.e. 350 to 550ºC) tensile tests have been found using the crosshead displacement of the tensile testing machine. This method was found to underestimate the % elongation values by, on average, 10 to 20% (from comparison of the tensile test results obtained using video extensometer at the same temperature and strain rate condition).

[0092] Figs. 26 and 27 show deformation behaviour of an FG sheet and a C sheet deformed at 350°C and strain rates of $5.0\mathrm{x}10^{-4}\ \mathrm{s}^{-1}$ (Fig. 26) and $6.7\mathrm{x}10^{-1}\ \mathrm{s}^{-1}$. (Fig. 27) Figs. 28 and 29 show deformation behaviour of FG sheets and C sheets at various temperatures. It is evident from Figures 18 through 20 that except in three cases of test temperatures and strain rates, the FG sheet achieves significantly higher % elongations at high temperatures, with more pronounced difference at 350ºC and 400ºC (i.e. temperatures of interest for warm forming operations). The two materials showed similar % elongation at 500°C and the strain rates of $6.7\mathrm{x}10^{-2}\ \mathrm{s}^{-1}$ and $6.7\mathrm{x}10^{-1}\ \mathrm{s}^{-1}$ and at 550°C and the strain rate of $6.7\mathrm{x}10^{-1}\ \mathrm{s}^{-1}$. These results reflect the FG sheet's high potential for future cost-effective warm forming operations in a wide range of strain rates and temperatures. The highest % elongation of approximately 290% (measured using a video extensometer) achieved at 500ºC and strain rate of $2.0\mathrm{x}10^{-2}\ \mathrm{s}^{-1}$ (this is a much higher strain rate than the one reported for the superplastic sheet formed in U.S. Patent No. 6,350,329, mentioned above (i.e. 370% at a strain rate of $5.0\mathrm{x}10^{-4}\ \mathrm{s}^{-1}$), meaning that the current material may be attractive to the automotive industry for cost-effective production of panels). The increase in, or retaining the same, % elongation with increasing strain rate also suggest that the high ductility of the FG sheet can be maintained even at strain rates higher than the highest rate studied here. This can potentially facilitate ultra-fast warm forming operations of FG AA6xxx sheets (it is believed that this has not been previously achieved).

[0093] Cavitation and fracture behaviour

[0094] Figs. 32 and 33 show optical microscopy images (through-thickness cross section) of deformed (i.e. tensile tested) and fractured samples of the FG sheet (Fig. 33) and a C sheet (Fig. 32) at 350°C and a strain rate of $5.0\text{x}10^{-4}\text{s}^{-1}$. The FG materials have shown more effective and uniform thinning to the fracture surface (which appears as a point when viewing through-thickness cross section). The C sheet has a rugged through-thickness fracture profile, demonstrating the inferior deformation to fracture behaviour. The FG material has also shown, generally, a higher resistance to cavitation during deformation, particularly when deformed at low strain rates and 500°C. This is demonstrated in Figs. 34 (FG sheet) and 35 (C sheet), which show the optical microscopy images of the through-thickness cross sections of fractured tensile samples tested at 500°C and the strain rate of $5.0\text{x}10^{-4}\text{s}^{-1}$. The fracture surface analysis conducted using scanning electron microscopy (SEM) show further evidence for the resistance to void/cavity formation in the FG sheet, consistent with the observed higher % elongations for the FG sheet. Examples of the SEM fracture surfaces for the FG and C sheets are shown in Figs. 23 (C sheet) and 24 (FG sheet). The implication of the resistance to void/cavity formation in the FG sheet during deformation is that the sheet will not prematurely fail during high temperature forming to produce products such as automotive panels, while extensive void formation can potentially happen in the C sheet if it is used for similar high temperature operations.

[0095] Another difference in the properties of the FG sheet with the C sheet is in achieving large % elongations without encountering premature failure due to the effect of precipitate network at the grain boundaries and the associated precipitate-free zones (PFZ). In other words, contrary to the C sheet, as the grain boundaries of the FG sheet are practically free from any precipitation network, the FG sheet will not be prone (or will be less prone) to pre-mature failure due stress concentration at the grain boundary precipitates, and/or grain boundary sliding interactions with precipitates and PFZ during high temperature deformation.

[0096] Further embodiments

[0097] Consistent with the results obtained, embodiments of the instant invention include alloy sheets with one or more of the following properties:

average grain size: <40μm, <25μm, <20μm, <18μm, <16μm, <14μm, or <12μm; and

ductility according to one or any combination of the elongation % values in Table 1.

[0098] Table 1: Elongation values at particular strain rates and temperatures.

	0.0005 s^{-1}	0.001 s^{-1}	0.01 s^{-1}	0.1 s^{-1}	0.67 s^{-1}
350°C	>125%	>110%	>75%	>100%	>110%
400°C	>125%	>125%	>100%	>100%	>125%
450°C	>130%	>130%	>150%	>125%	>170%
500°C	>150%	>150%	>170%	>170%	>170%
550°C	>150%	>125%	>175%	>170%	>175%

[0099] -ductility of greater than 80% elongation at 350°C to 550°C (including individually at 350°C, 400 °C, 450 °C, 500 °C, and 550°C) at and a strain rate of $5x10^{-4}s^{-1}$ to $6.7x10^{-1}s^{-1}$ (including individually at $5x10^{-4}s^{-1}$, $2.0x10^{-3}s^{-1}$, $2.0x10^{-2}s^{-1}$, $6.7x10^{-2}s^{-1}$, and $6.7x10^{-1}s^{-1}$), and any combination of these individual values; and

[00100] -grain stability quantified by an increase in average grain size: (a) of less than 200% or less than 100% over one hour at 550°C, (b), less than 20% or less than 10% over one hour at 400°C, (c) less than 100% or less than 50% over one hour at 500°C, or (d) less than 40% or less than 20% over one hour at 450°C, or any combination thereof.

[00101] AA6111

[00102] The process has also been applied to AA6111 (ROUTE A1). The grain size measurement on the planar section provided an average grain size of 20.2 microns. The comparable commercial alloy of AA6111 has an average grain size in the range of 30 to 45 microns. Thus, this thermomechanical process has resulted in grain refining.

[00103] In the preceding description, for purposes of explanation, numerous details are set forth in order to provide a thorough understanding of the embodiments of the invention. However, it will be apparent to one skilled in the art that these specific details are not required in order to practice the invention.

[00104] The above-described embodiments of the invention are intended to be examples only. Alterations, modifications and variations can be effected to the particular embodiments by those of skill in the art without departing from the scope of the invention, which is defined solely by the claims appended hereto.

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What is claimed is:

1. A process of imparting a fine grain structure to a heat treatable alloy, the process comprising:

providing a heat treatable alloy having a precipitating constituent;

solution heat treating the alloy;

cooling the alloy to form a supersaturated solid solution;

plastically deforming the alloy to form a dispersed high-energy defect structure for subsequent (a) dispersed nucleation of recrystallization, or (b) dispersed recovery-recrystallization, or both (a) and (b), and to form dispersed fine precipitates;

heating the alloy below a recrystallization temperature with a time-temperature profile to continue to form dispersed fine precipitates; and

heating the alloy at or above the recrystallization temperature to effect (a) dispersed nucleation of recrystallization and growth of nuclei, or (b) dispersed recovery-recrystallization, or both (a) and (b), to thereby form a fine grain structure.

2. The process of claim 1, the alloy is non-isothermally heated to a temperature that is at or above the recrystallization temperature and then is isothermally heated at the temperature at or above the recrystallization temperature.

3. The process of claim 1, wherein the heating below the recrystallization temperature and the heating at or above the recrystallization temperature both consist essentially of non-isothermal heating.

4. The process of claim 1, wherein the heating below the recrystallization temperature comprises a mixture of non-isothermal heating and isothermal heating.

5. The process of claim 1, wherein the heating below the recrystallization temperature is heating below 300°C.

6. The process of claim 1, wherein the heating at or above the recrystallization temperature is heating at or above 300°C.

7. The process of claim 1, wherein the fine grain structure is achieved in the absence of further plastic deformation after the heating below the recrystallization temperature.

8. The process of claim 1, wherein the alloy is an aluminum alloy.

9. The process of claim 8, wherein the alloy is an AA6xxx alloy.

10. The process of claim 8, wherein the alloy is an AA6xxx alloy with or without additional incidental or minor alloying elements.

11. The process of claim 8, wherein the alloy is a multi- or bi-layered material, wherein at least one layer comprises an AA6xxx alloy and at least one other layer comprises another aluminum alloy.

12. The process of claim 11, wherein the another aluminum alloy is a AA1xxx or AA3xxx alloy.

13. The process of claim 8, wherein the alloy is an AA6451, AA6111, AA6013, AA6061, AA6063, or AA6066 alloy.

14. The process of claim 8, wherein the alloy is AA6451 or a Cu-free version of AA6451.

15. The process of claim 1, wherein the alloy is a heat treatable titanium, magnesium, cobalt, copper, or nickel alloy.

16. The process of claim 1, wherein the cooling prior to plastically deforming comprises quenching.

17. The process of claim 1, wherein the plastically deforming comprises cold rolling.

18. The process of claim 17, wherein the plastically deforming comprises cold rolling the alloy with a reduction of at least 50%.

19. The process of claim 1, wherein between the cooling which follows the solution heat treating and the plastically deforming, the process further comprises naturally aging the alloy.

20. The process of claim 1, wherein the alloy is heated continuously to or above the recrystallization temperature.

21. The process of claim 1, further comprising, after heating at or above the recrystallization temperature, cooling the alloy or allowing the alloy to cool.

22. The process of claim 1, wherein:

the alloy is AA6451 or a Cu-free version of AA6451;

the plastically deforming comprises cold rolling the alloy with a reduction of at least 50%;

the alloy is non-isothermally heated at a rate of less than 40°C/s to a temperature that is at or above the recrystallization temperature and then is isothermally or non-isothermally heated at the temperature at or above the recrystallization temperature; and

the average grain size of the fine grain structure is less than 25μm;

and further comprising, after heating at or above the recrystallization temperature, cooling the alloy or allowing the alloy to cool.

23. An alloy sheet produced by the process of claim 1.

24. The alloy sheet of claim 23, wherein the alloy sheet comprises the following properties:

a ductility of greater than 80% elongation at 350°C to 550°C and a strain rate of $5\times10^{-4}s^{-1}$ to $6.7\times10^{-1}s^{-1}$;

an average grain size of less than 25μm; and

a grain stability, quantified by an increase in average grain size of less than 100% over one hour at 550°C, and an increase in average grain size of less than 10% over one hour at 400°C.

25. An AA6xxx alloy sheet comprising the following properties:

a ductility of greater than 80% elongation at 350°C to 550°C and a strain rate of $5\times10^{-4}s^{-1}$ to $6.7\times10^{-1}s^{-1}$;

an average grain size of less than 25μm; and

a grain stability, quantified by an increase in average grain size of less than 100% over one hour at 550°C, and an increase in average grain size of less than 10% over one hour at 400°C.

26. An AA6xxx alloy sheet comprising the following properties:

a ductility of greater than 80% elongation at 350°C to 550°C and a strain rate of $5x10^{-4}s^{-1}$ to $6.7x10^{-1}s^{-1}$;

an average grain size of less than 25μm; and

a substantially uniform precipitate distribution below solvus temperature with precipitates substantially in one of more of the following shapes: oval, rounded, and cuboid.

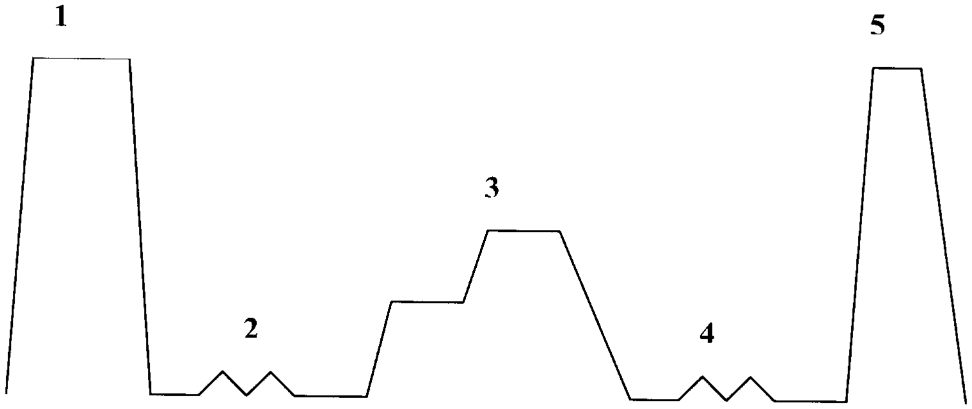


Fig. 1

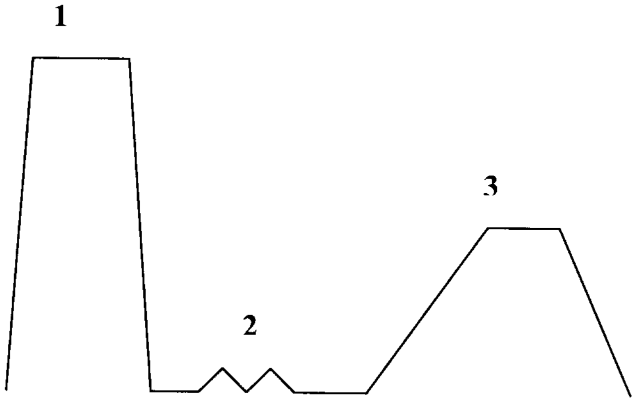


Fig. 2

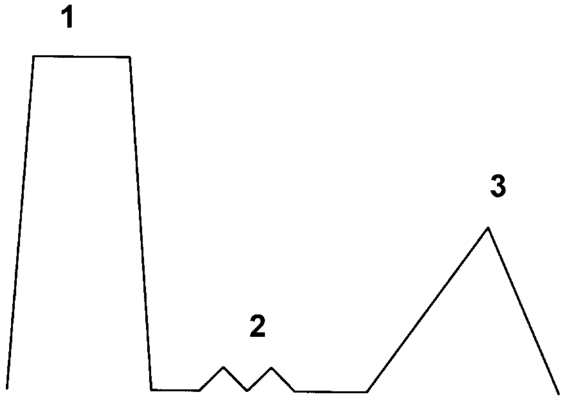


Fig. 3

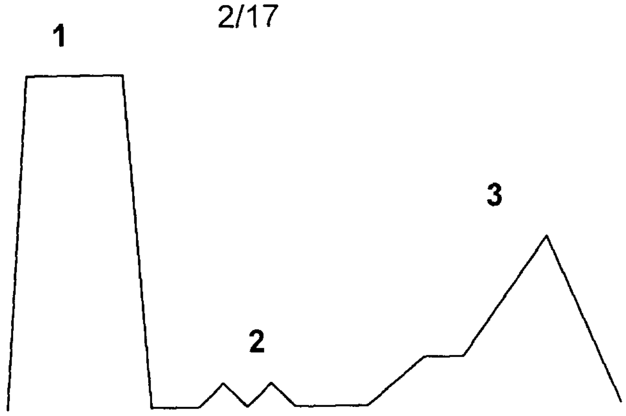


Fig. 4

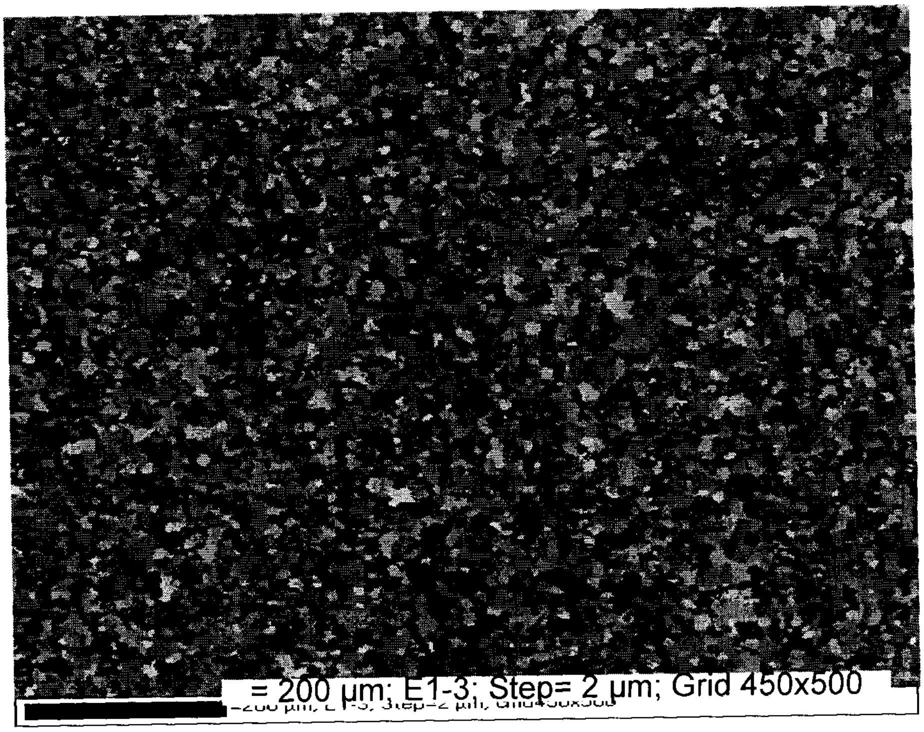


Fig. 5

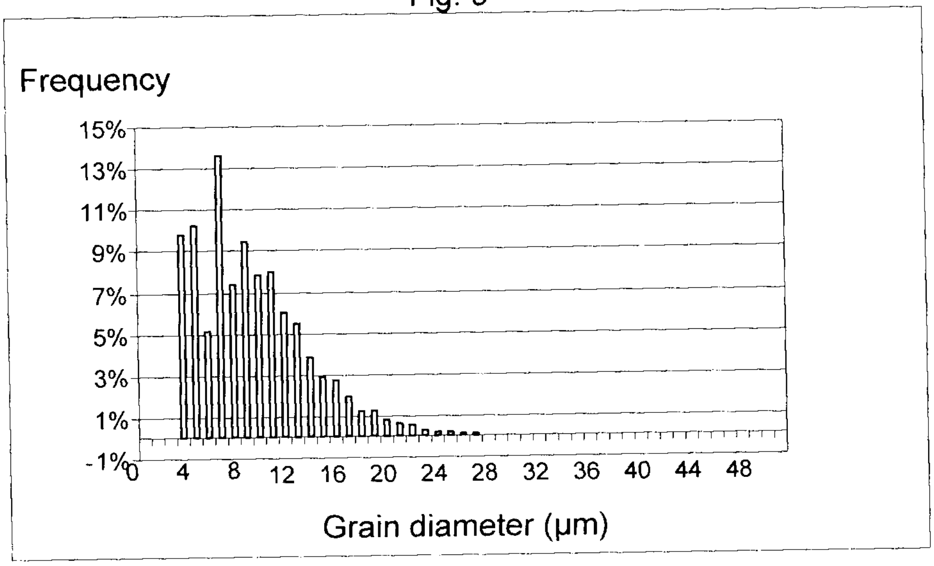


Fig. 6

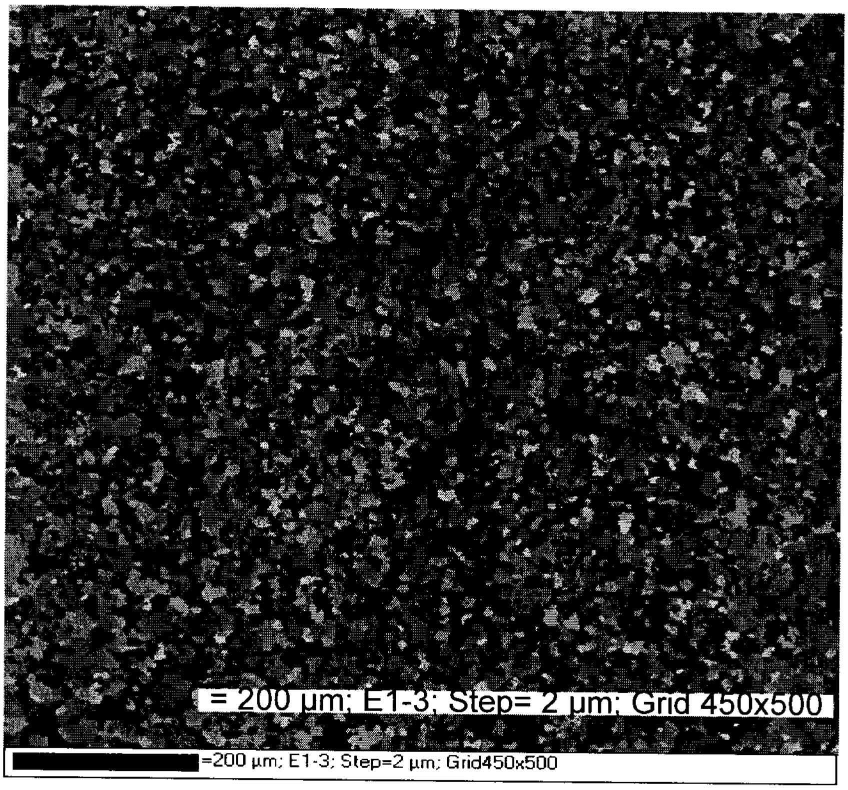


Fig. 7

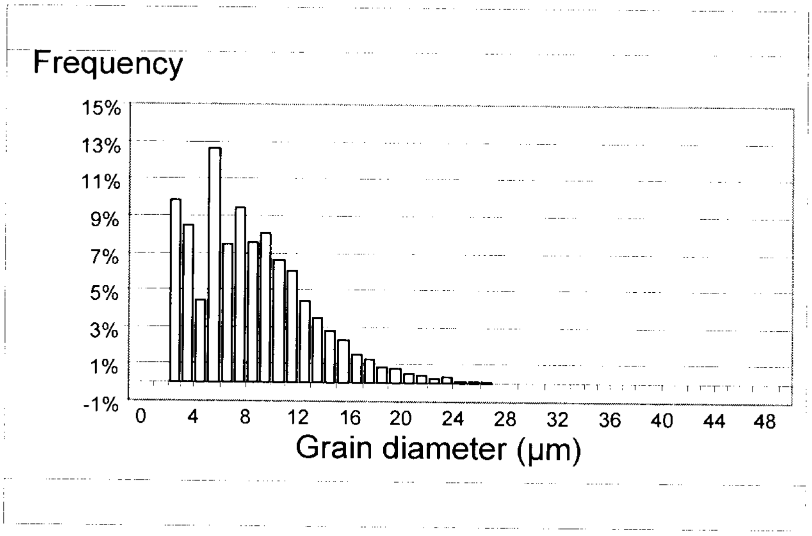


Fig. 8

Fig. 9

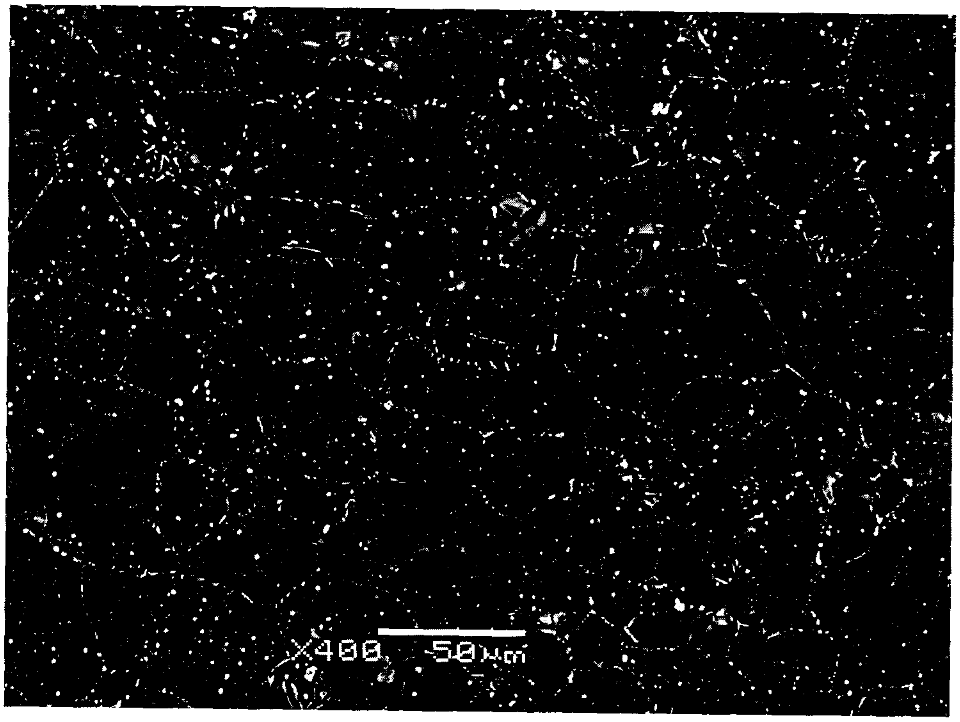


Fig. 10

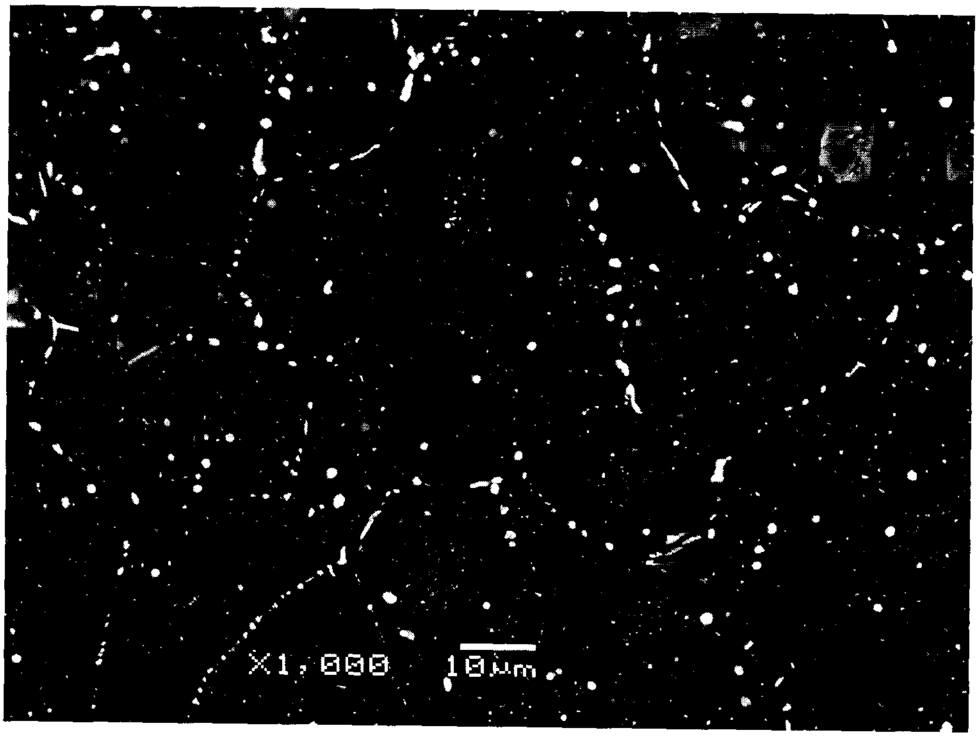
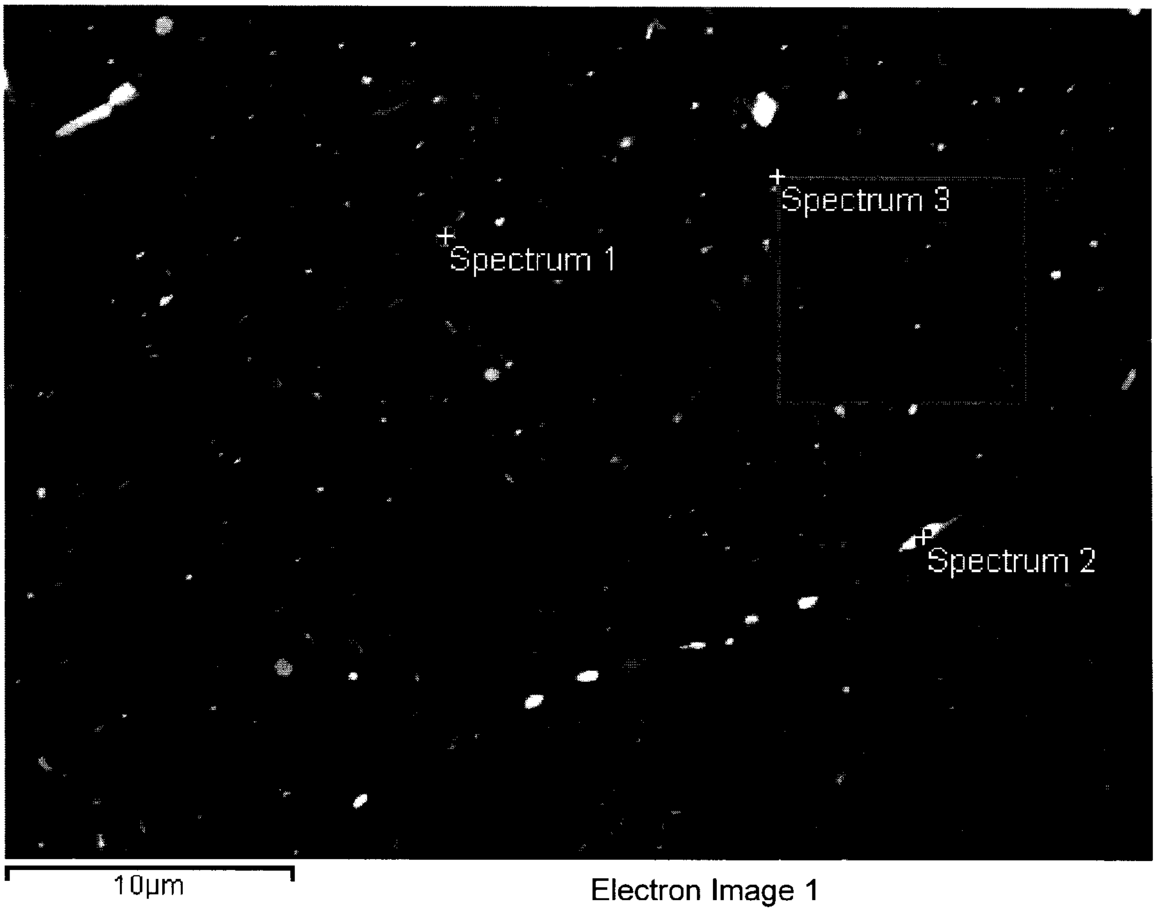


Fig. 11



Average Composition (weight %)	Si	Cu	O	Al
Spectrum 1 (Block Particle)	3.19	0	9.99	Bal
Spectrum 2 (Particle on grain boundary)	2.71	7.19	7.03	Bal
Spectrum 3	0	0	0	100%

Fig. 12

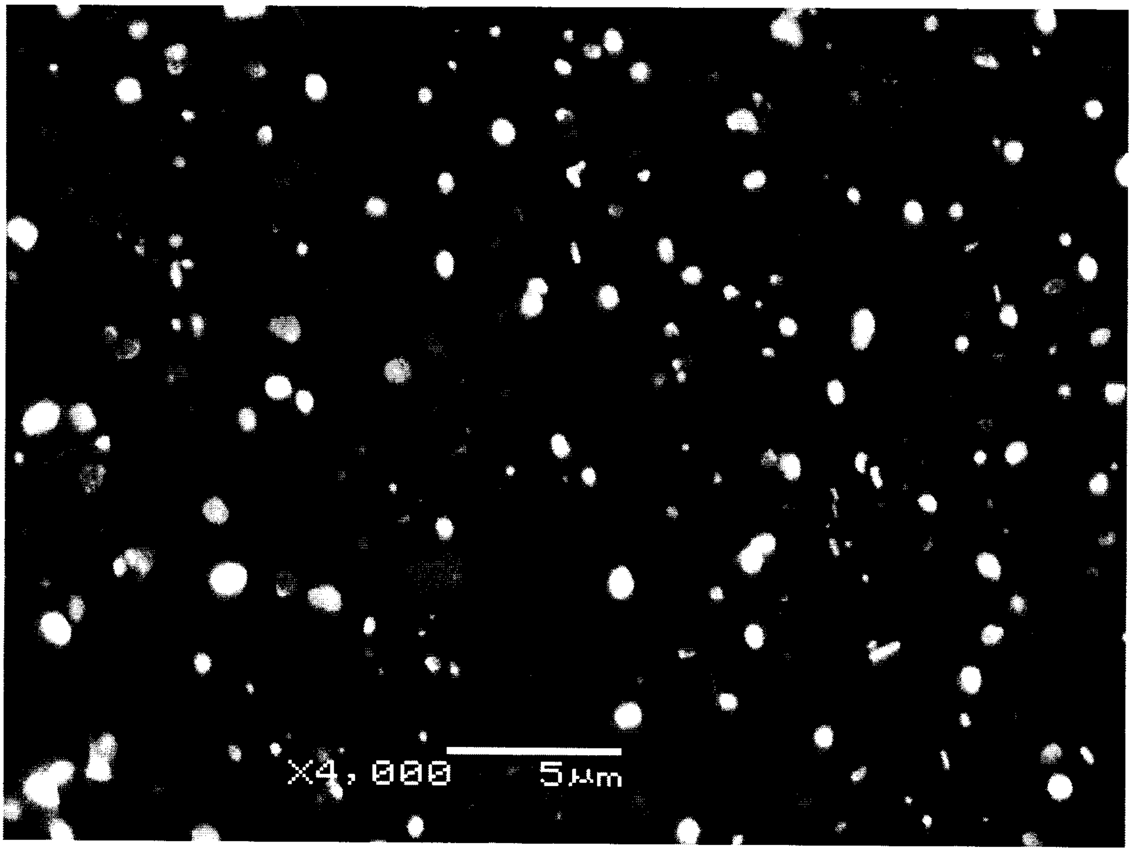


Fig. 13

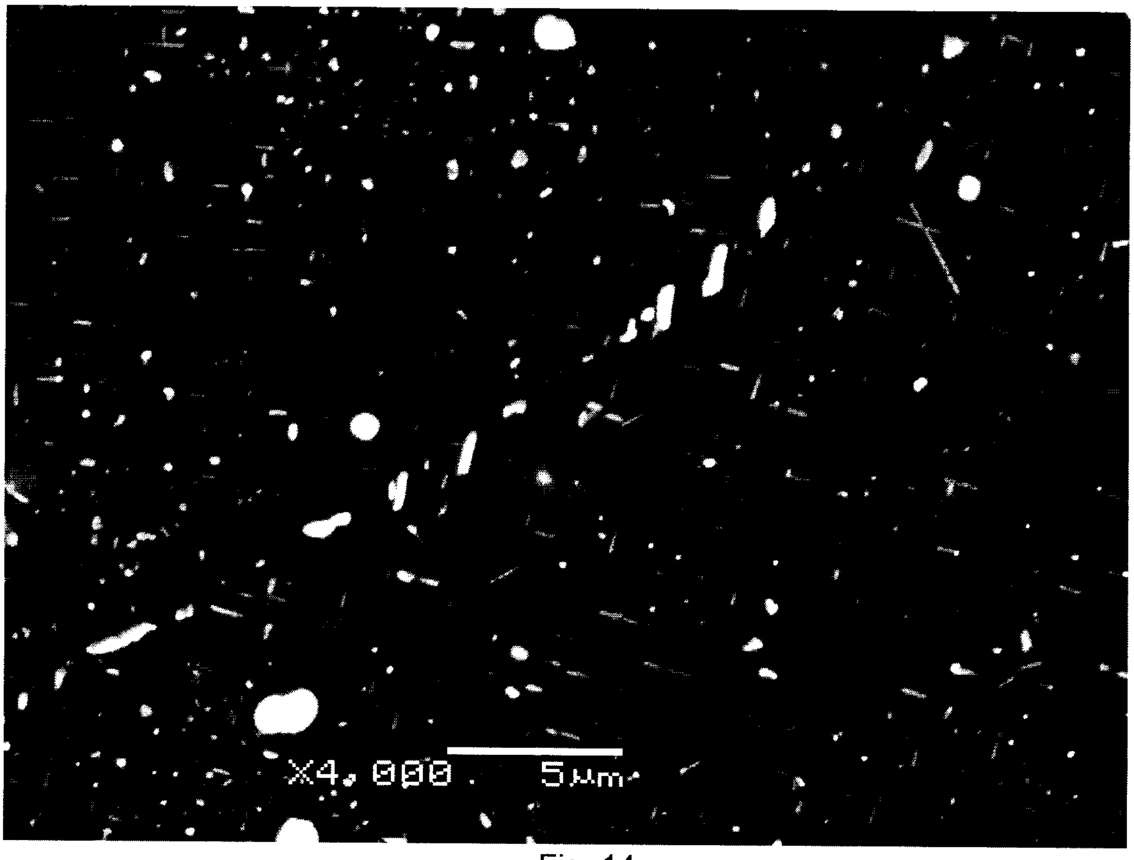


Fig. 14

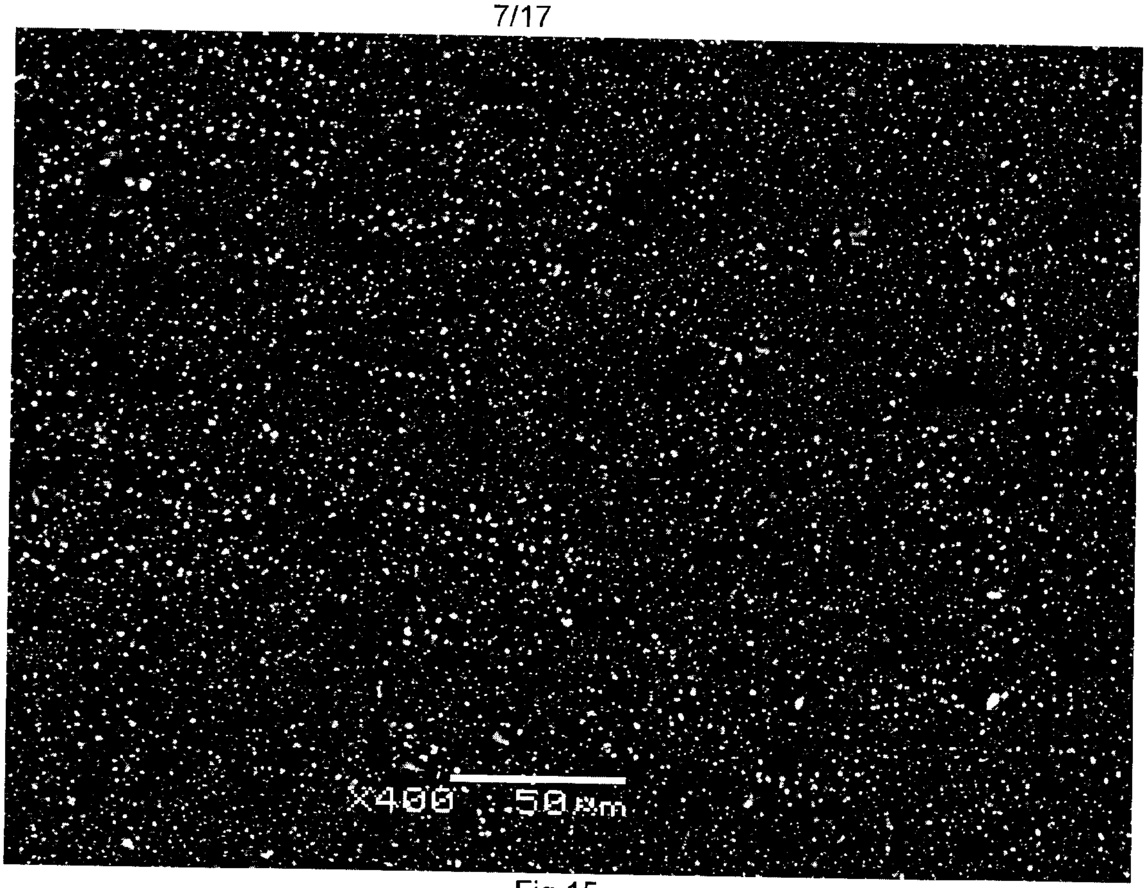


Fig.15

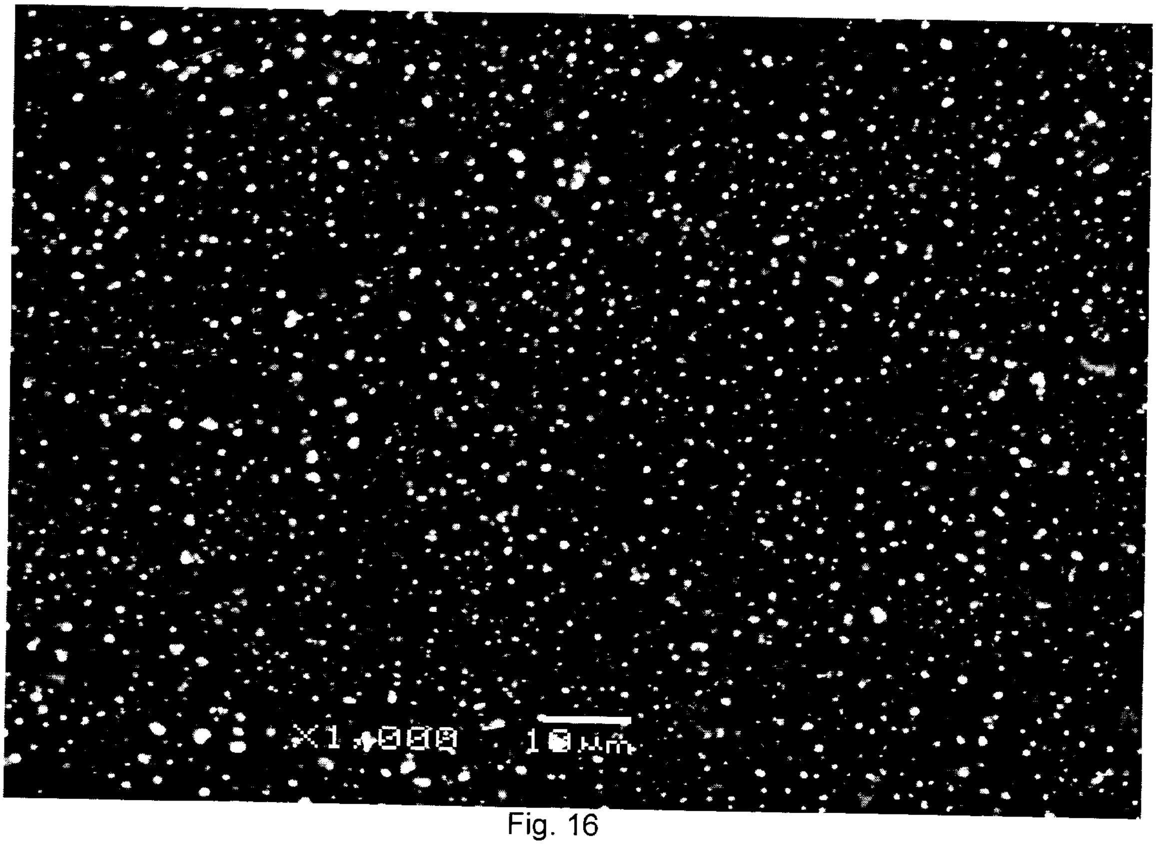


Fig. 16

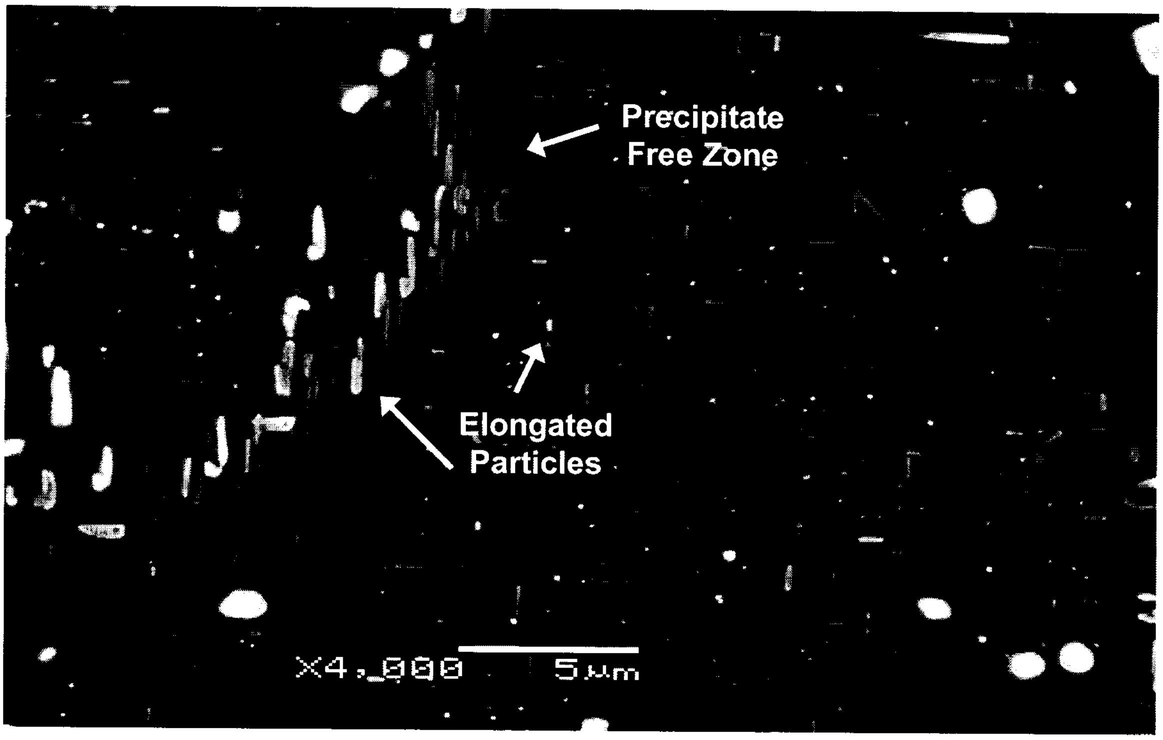

Precipitate Free Zone
Elongated Particles
X4,000
5μm

Fig. 17

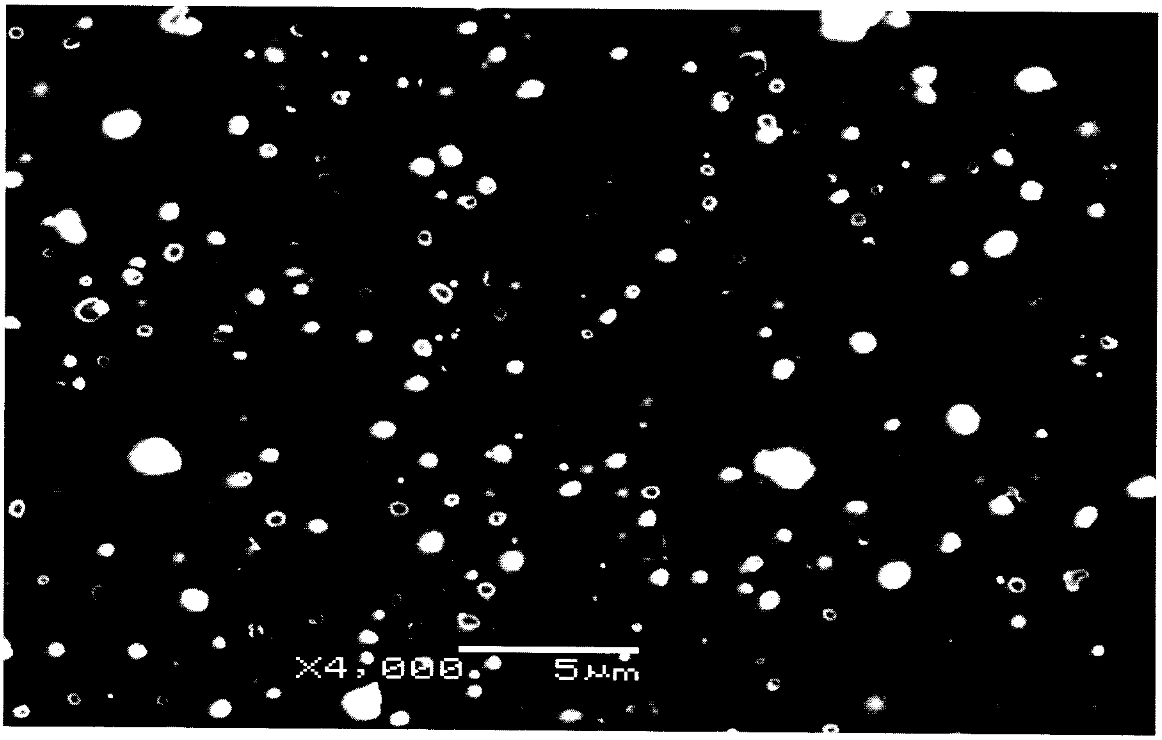

X4,000
5μm

Fig. 18

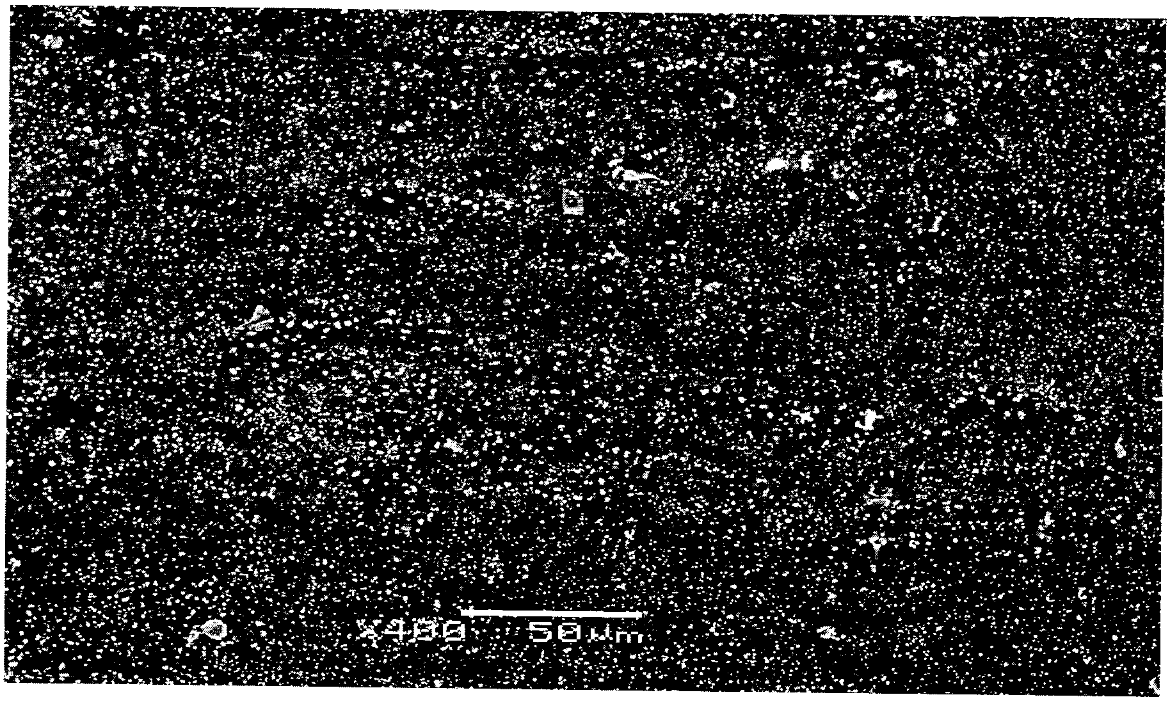


Fig. 19

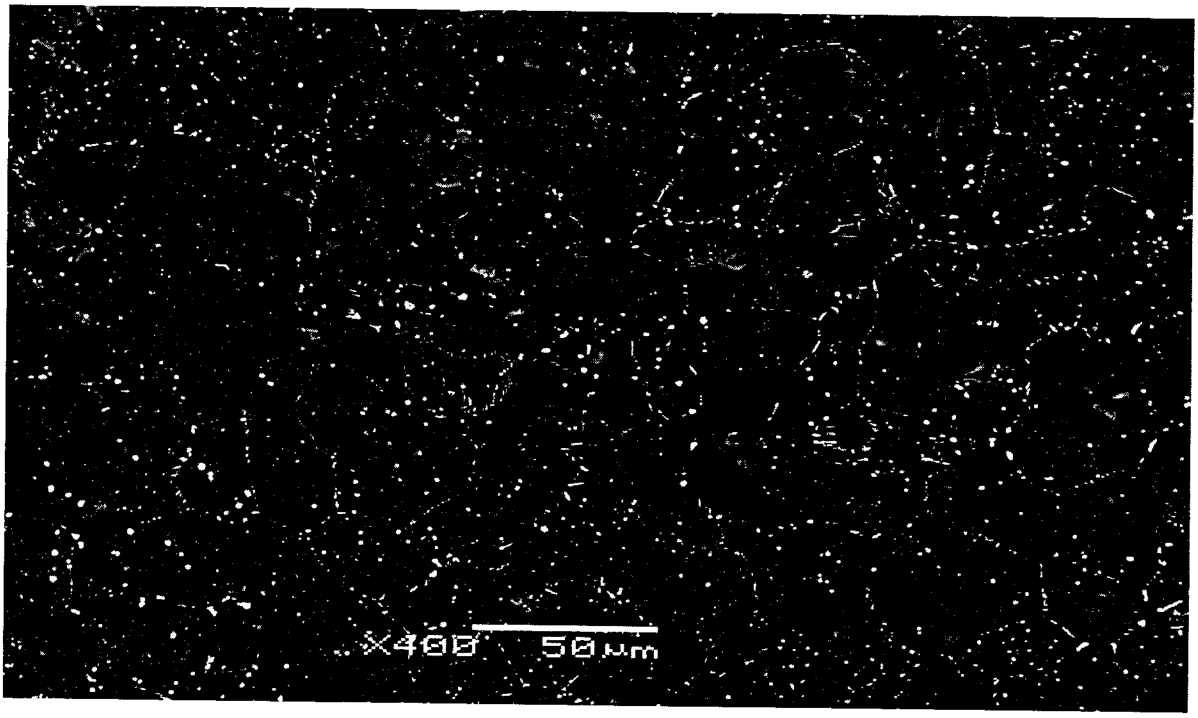


Fig. 20

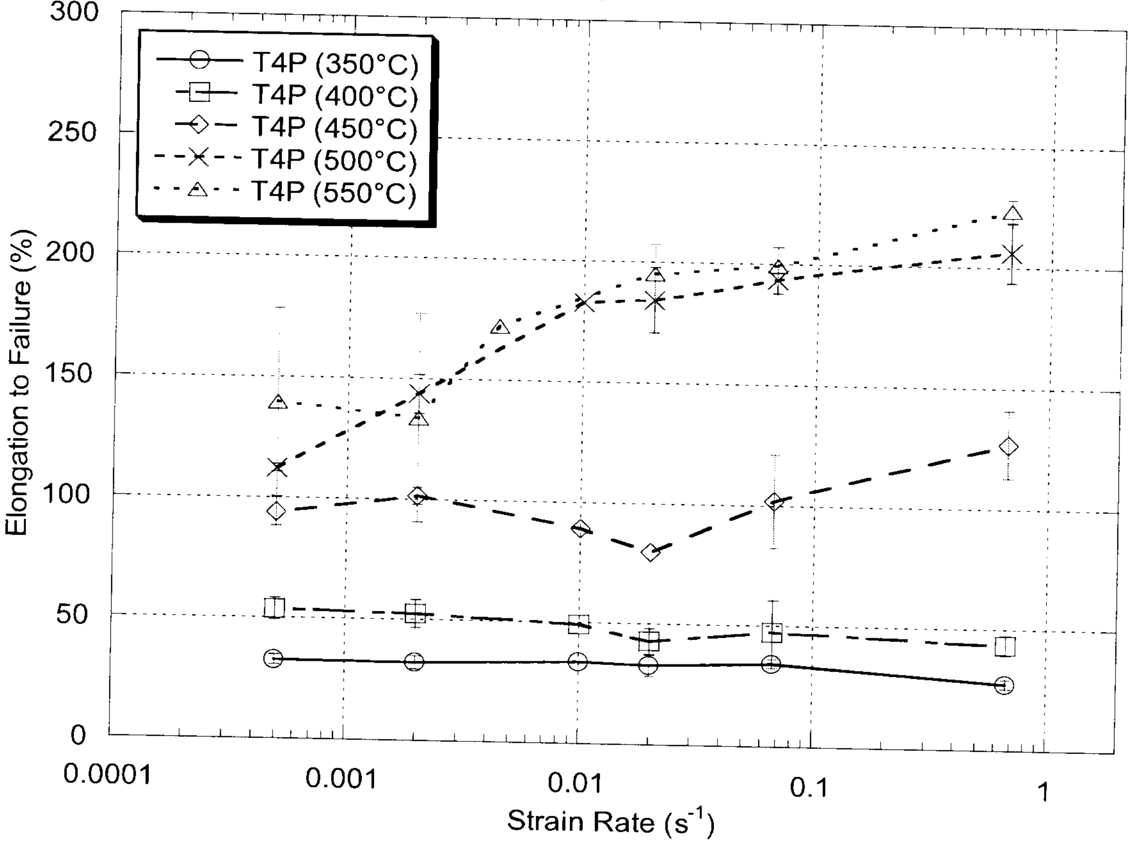

T4P (350°C)
T4P (400°C)
T4P (450°C)
T4P (500°C)
T4P (550°C)
Elongation to Failure (%)
0
50
100
150
200
250
300
0.0001
0.001
0.01
0.1
1
Strain Rate (s^{-1})

Fig. 21

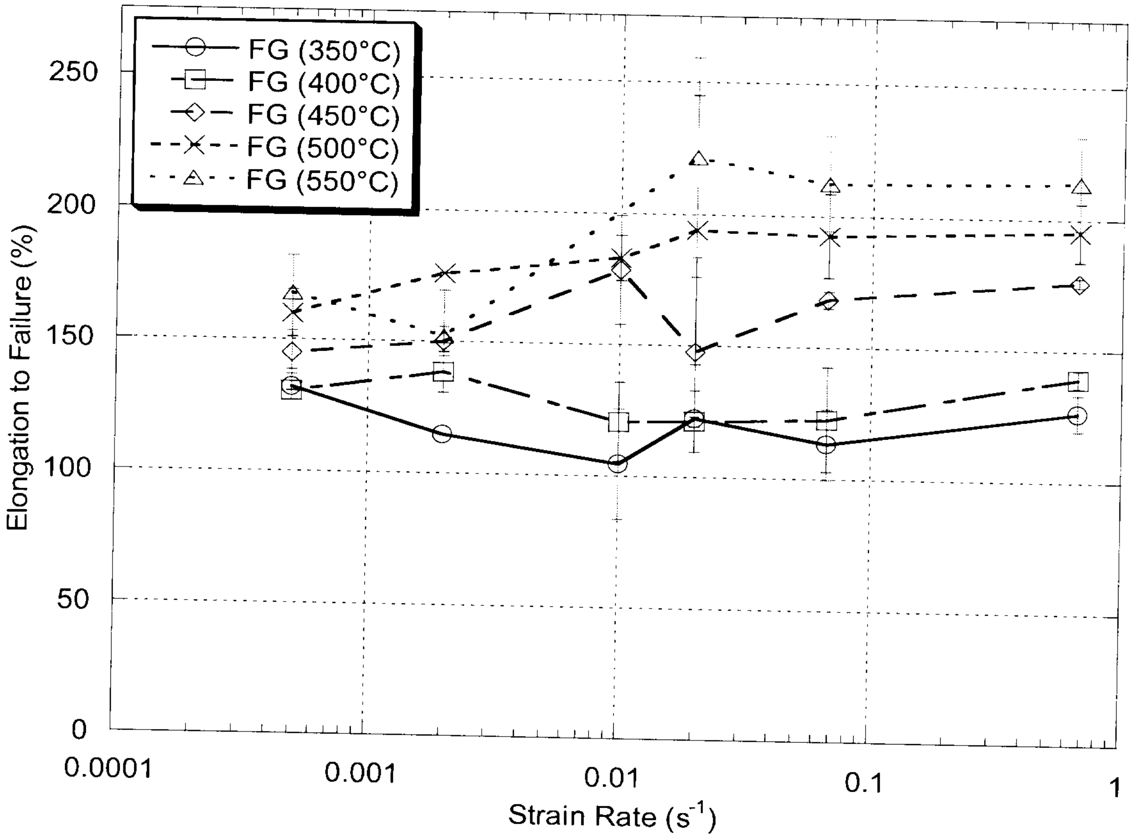

FG (350°C)
FG (400°C)
FG (450°C)
FG (500°C)
FG (550°C)
Elongation to Failure (%)
0
50
100
150
200
250
0.0001
0.001
0.01
0.1
1
Strain Rate (s^{-1})

Fig. 22

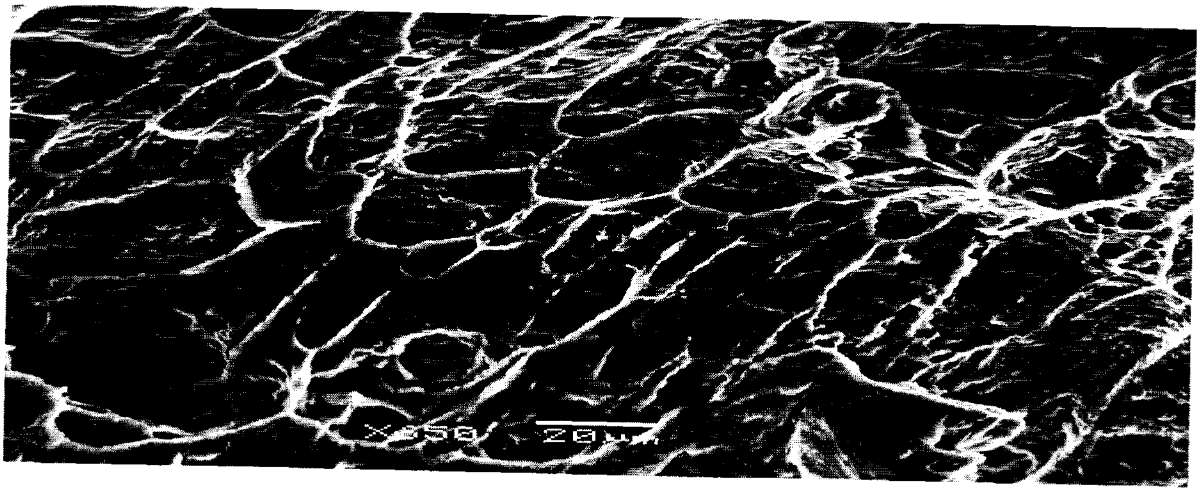


Fig. 23

Fig. 24

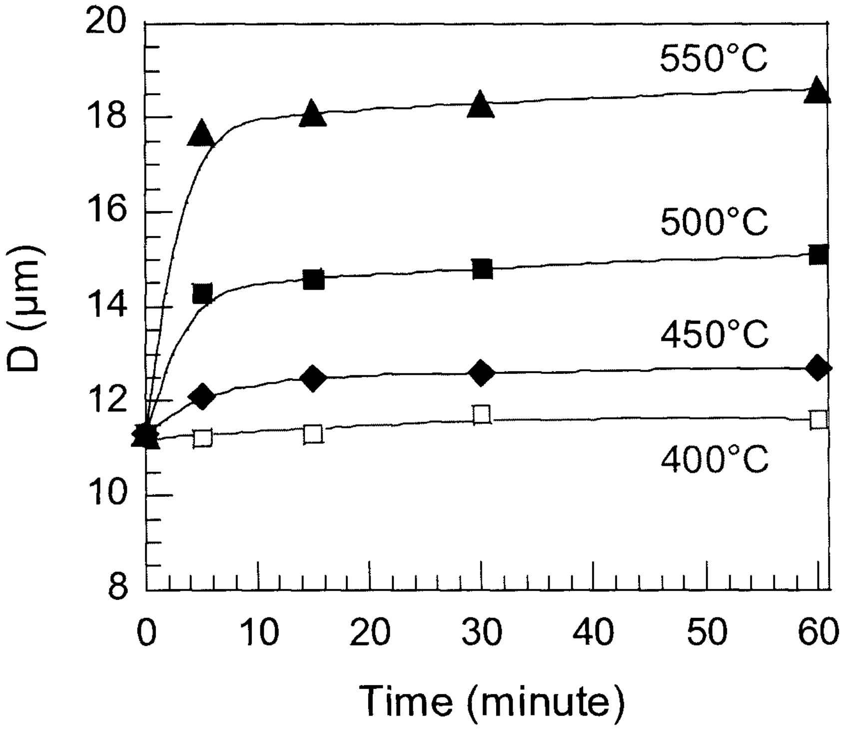

20
18
16
14
12
10
8
D (µm)
0
10
20
30
40
50
60
Time (minute)
550°C
500°C
450°C
400°C

Fig. 25

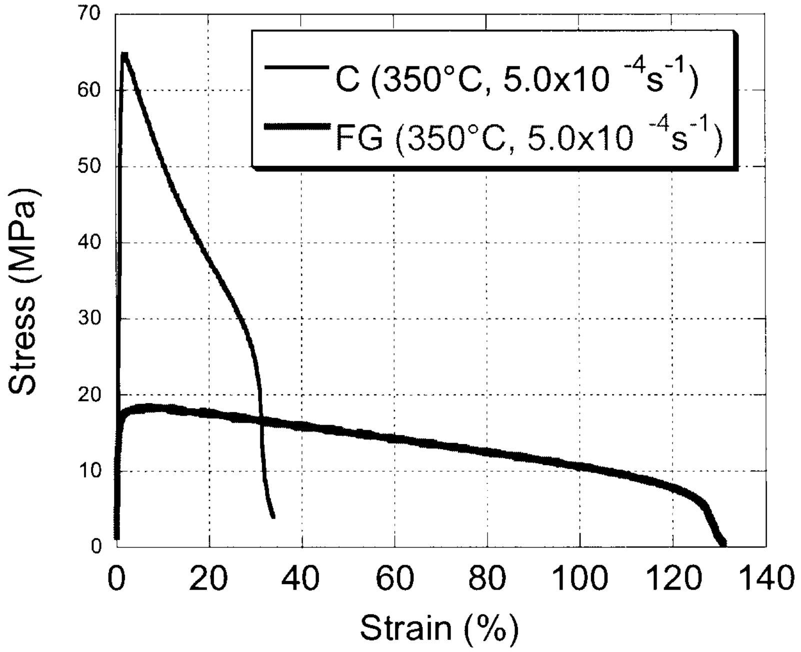

70
60
50
40
30
20
10
0
Stress (MPa)
0
20
40
60
80
100
120
140
Strain (%)
C (350°C, 5.0x10 -4s-1)
FG (350°C, 5.0x10 -4s-1)

Fig. 26

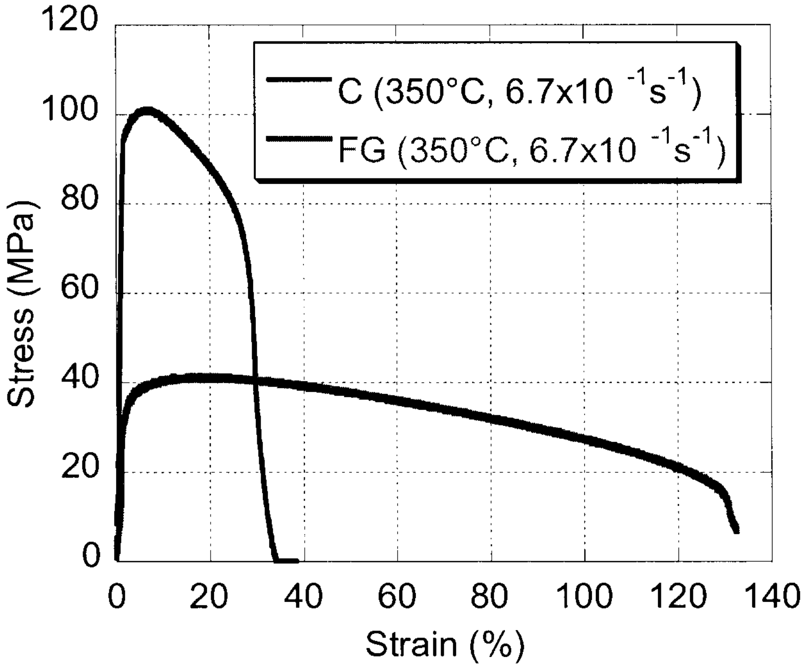

120
100
80
60
40
20
0
Stress (MPa)
0
20
40
60
80
100
120
140
Strain (%)
C (350°C, 6.7x10 -1s-1)
FG (350°C, 6.7x10 -1s-1)

Fig. 27

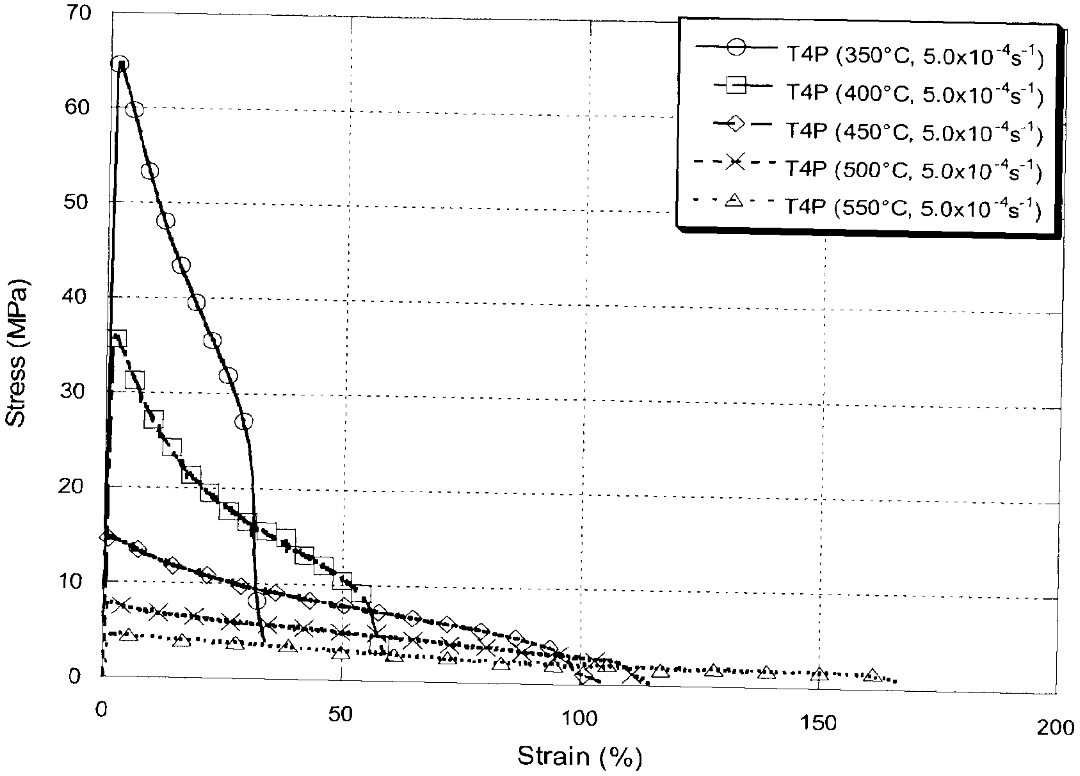

T4P (350°C, 5.0x10⁻⁴s⁻¹)
T4P (400°C, 5.0x10⁻⁴s⁻¹)
T4P (450°C, 5.0x10⁻⁴s⁻¹)
T4P (500°C, 5.0x10⁻⁴s⁻¹)
T4P (550°C, 5.0x10⁻⁴s⁻¹)
Stress (MPa)
0
10
20
30
40
50
60
70
Strain (%)
0
50
100
150
200

Fig. 28

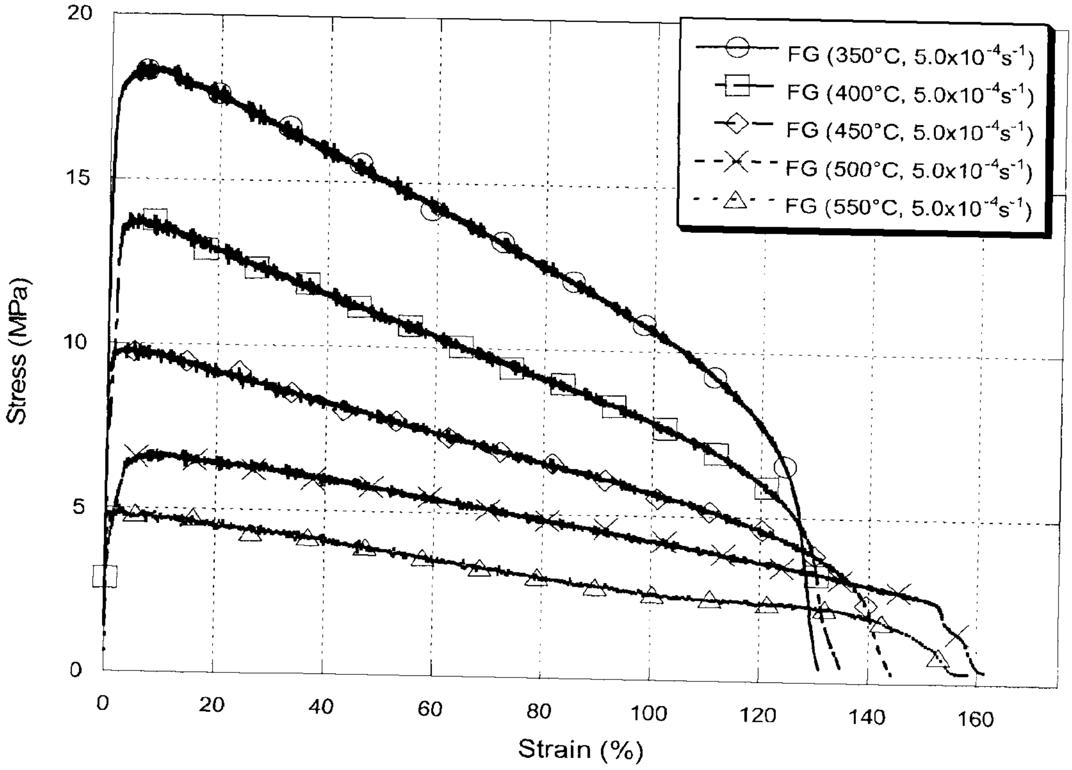

FG (350°C, 5.0x10⁻⁴s⁻¹)
FG (400°C, 5.0x10⁻⁴s⁻¹)
FG (450°C, 5.0x10⁻⁴s⁻¹)
FG (500°C, 5.0x10⁻⁴s⁻¹)
FG (550°C, 5.0x10⁻⁴s⁻¹)
Stress (MPa)
0
5
10
15
20
Strain (%)
0
20
40
60
80
100
120
140
160

Fig.29

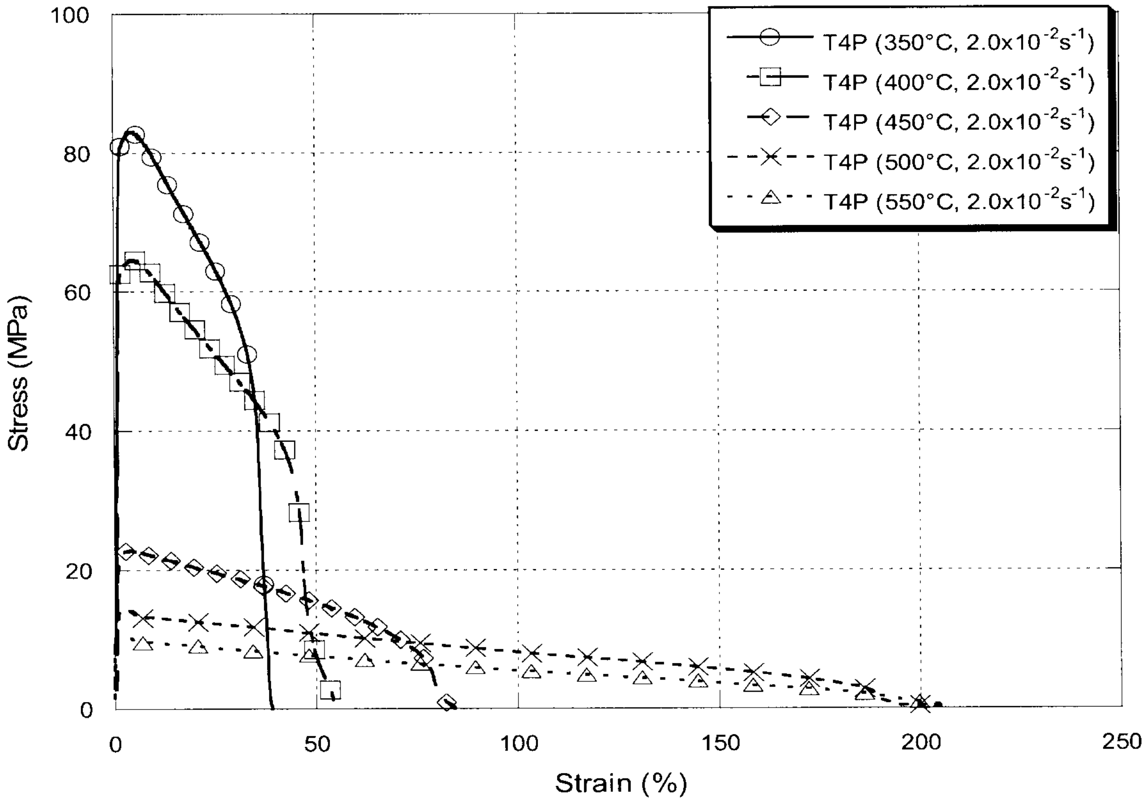

T4P (350°C, 2.0x10^{-2}s^{-1})
T4P (400°C, 2.0x10^{-2}s^{-1})
T4P (450°C, 2.0x10^{-2}s^{-1})
T4P (500°C, 2.0x10^{-2}s^{-1})
T4P (550°C, 2.0x10^{-2}s^{-1})
Stress (MPa)
100
80
60
40
20
0
0
50
100
150
200
250
Strain (%)

Fig. 30

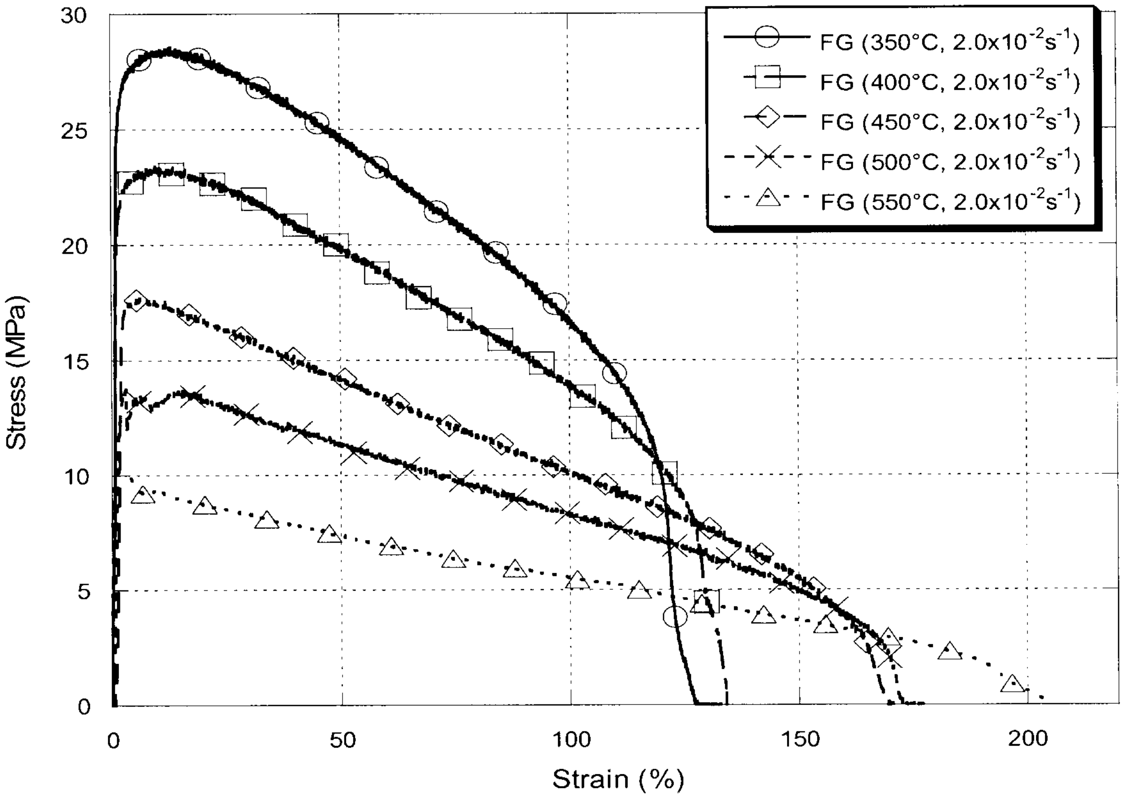

FG (350°C, 2.0x10^{-2}s^{-1})
FG (400°C, 2.0x10^{-2}s^{-1})
FG (450°C, 2.0x10^{-2}s^{-1})
FG (500°C, 2.0x10^{-2}s^{-1})
FG (550°C, 2.0x10^{-2}s^{-1})
Stress (MPa)
30
25
20
15
10
5
0
0
50
100
150
200
Strain (%)

Fig. 31

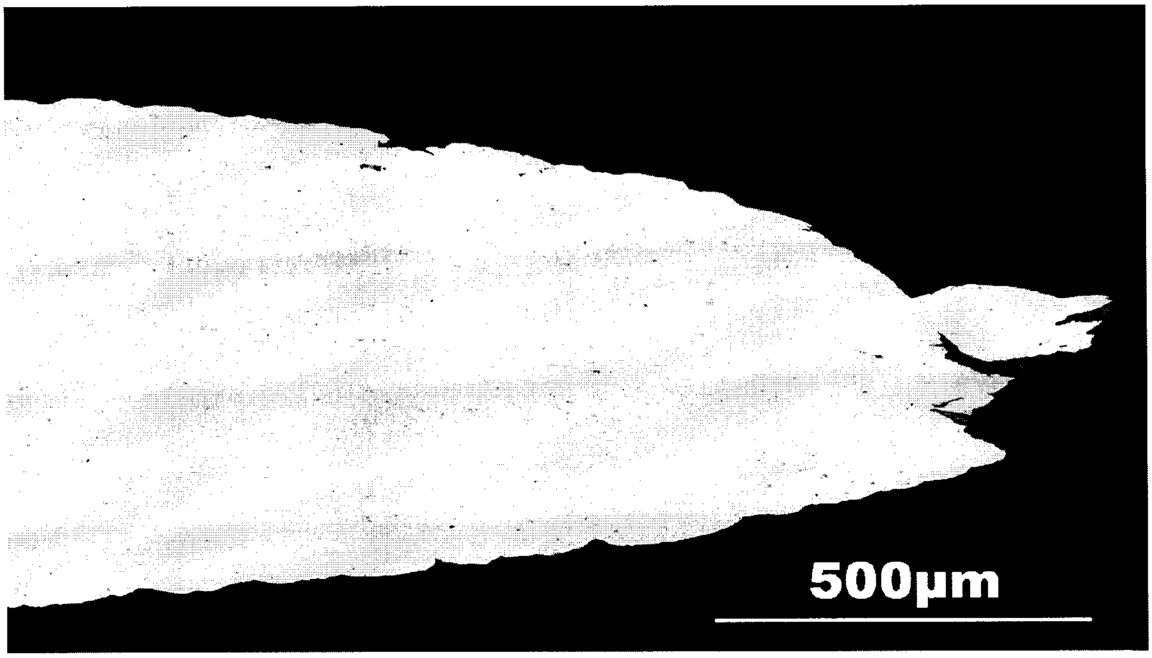


Fig. 32

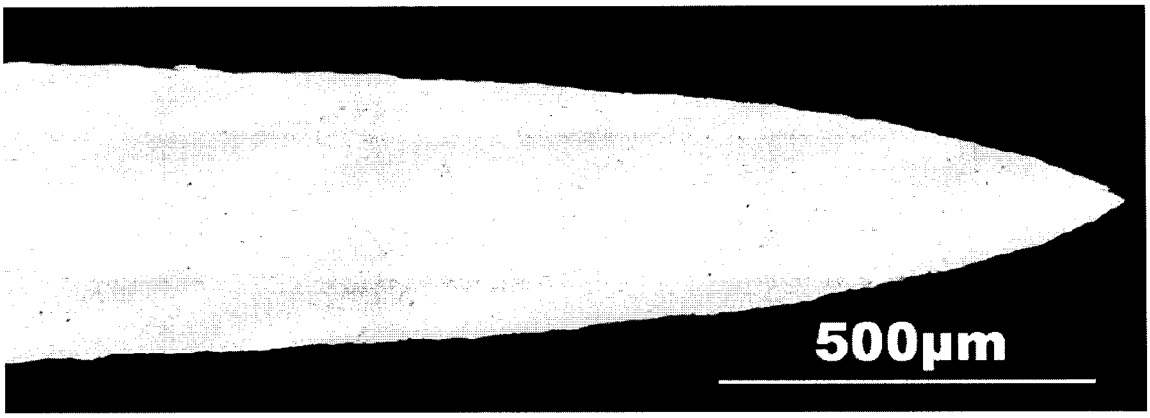


Fig. 33

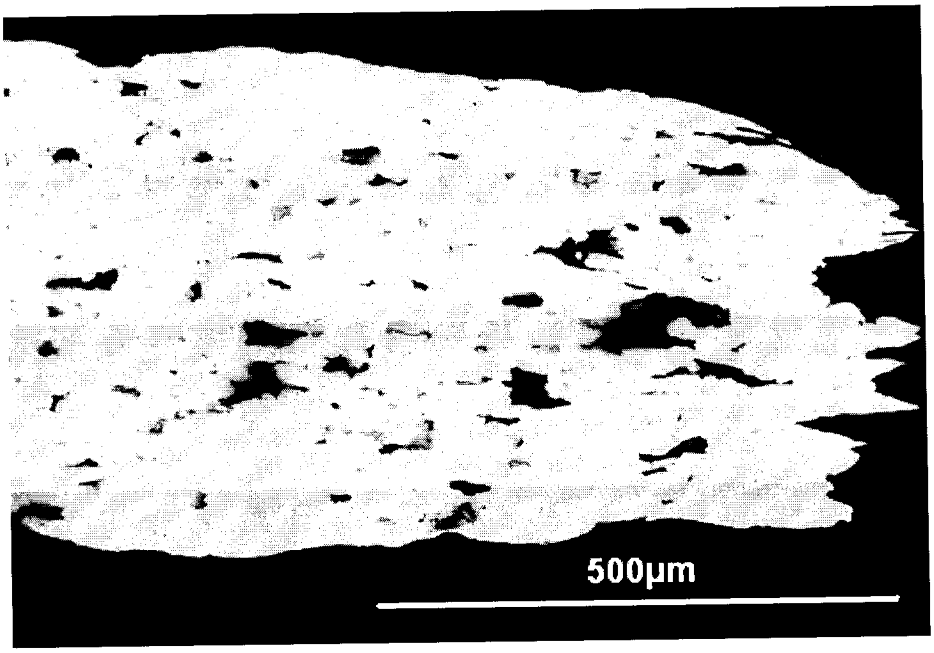


Fig. 34

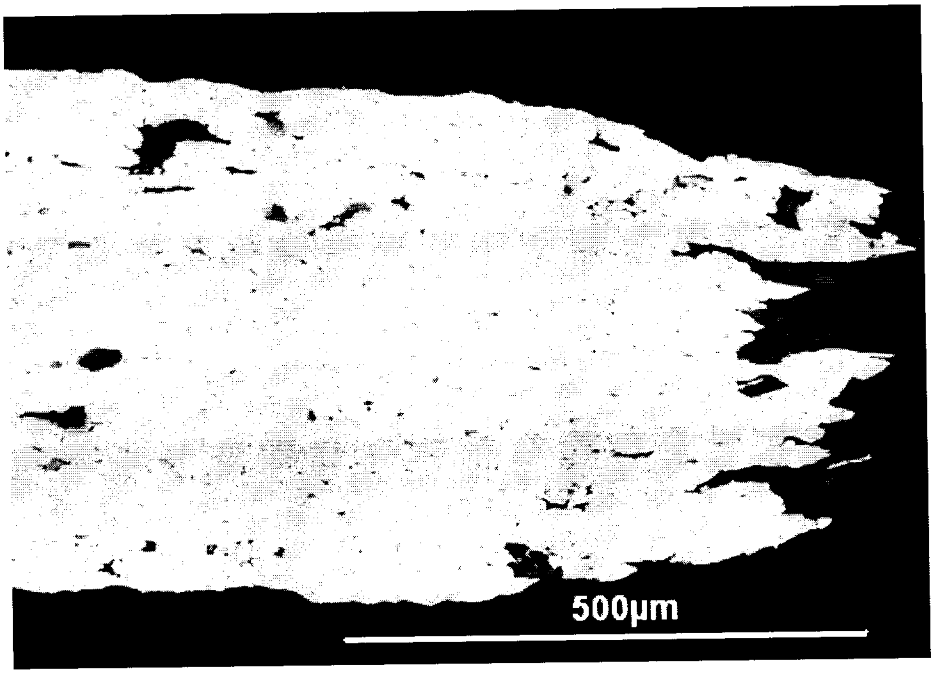


Fig. 35

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2009/000560

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***C22F 1/04*** (2006.01) , ***C22F 1/00*** (2006.01) , *B22D 21/04* (2006.01)
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)
IPC: C22F 1/04 (2006.01)

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Delphion, Qpat, Canadian Patent database, ScienceDirect and Scopus.
Keywords: aluminium, recrystallization, grain, fine, heat* and alloy.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,092,181 (Paton et al.) 30 may 1978 (30-05-1978) * whole document *	1, 5-10, 13, 14, 16-19-22
X	US 4,797,164 (Höllrigl et al.) 10 January 1989 (10-01-1989) * Col. 1, lines 55-68 and col. 2, lines 1-3 * * Col. 3, lines 3-7 *	1, 5-10, 13, 14, 16-18, 20-22
A	US 6,350,329 (Ttroeger et al.) 26 February 2002 (26-02-2002) * whole document *	1
A	US 4,722,754 (Ghosh et al.) 2 February 1988 (02-02-1988) * whole document *	1, 8-10 and 16-18

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

* Special categories of cited documents :

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

“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)

“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

“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

“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

“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

“&” document member of the same patent family

Date of the actual completion of the international search 17 July 2009 (17-07-2009)	Date of mailing of the international search report 20 July 2009 (20-07-2009)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476	Authorized officer Patrick Mamputu 819- 994-9537

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2009/000560

Box No. II **Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons :

1. [ ] Claim Nos. :
because they relate to subject matter not required to be searched by this Authority, namely :

2. [X] Claim Nos. : 23 and 24
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically :

Since the type of the alloy is not defined in claim 1, and the parameters will be dependent upon the nature of the alloy produced.

3. [ ] Claim Nos. :
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III **Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows :

1. [ ] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. [ ] As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos. :
4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos. :

Remark on Protest [ ] The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

[ ] The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

[ ] No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2009/000560

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US 4092181A	30-05-1978	AU 513778B2	18-12-1980
		AU 3538578A	01-11-1979
		CA 1098806A1	07-04-1981
		CH 638834A5	14-10-1983
		DE 2817978A1	02-11-1978
		DE 2817978C2	19-01-1989
		FR 2388893A1	24-11-1978
		FR 2388893B1	14-09-1984
		GB 1603573A	25-11-1981
		JP 1413265C	27-11-1987
		JP 53132420A	18-11-1978
		JP 61006141B	24-02-1986
		NO 149741B	05-03-1984
		NO 149741C	13-06-1984
		NO 781373A	26-10-1978
		US 4092181B1	01-01-1985
US 4797164A	10-01-1989	CA 1312262C	05-01-1993
		DE 3765611D1	22-11-1990
		EP 0263070A1	06-04-1988
		EP 0263070B1	17-10-1990
US 6350329B1	26-02-2002	AU 6381899A	17-01-2000
		US 6222380B1	24-04-2001
		US 2001023719A1	27-09-2001
		WO 0000653A1	06-01-2000
US 4486242A	04-12-1984	US 4528042A	09-07-1985