(19) World Intellectual Property Organization

International Bureau





(43) International Publication Date 6 May 2005 (06.05.2005)

PCT

(10) International Publication Number WO 2005/040445 A1

(51) International Patent Classification⁷:

C22F 3/00

(21) International Application Number:

PCT/CA2004/001877

- (22) International Filing Date: 26 October 2004 (26.10.2004)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

10/696,877

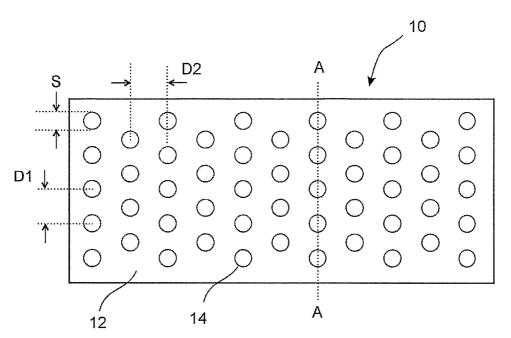
29 October 2003 (29.10.2003) U-

- (71) Applicant (for all designated States except US): ALCAN INTERNATIONAL LIMITED [CA/CA]; 1188 Sherbrooke Street West, Montreal, Québec H3A 3G2 (CA).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): LLOYD, David James [CA/CA]; 106 Nicholson's Point, R.R. #3, Bath, Ontario K0H 1G0 (CA).

- (74) Agents: GALE, Edwin, J. et al.; KIRBY EADES GALE BAKER, Box 3432, Station D., Ottawa, Ontario K1P 6N9 (CA).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: FUNCTIONALLY GRADED ALUMINUM ALLOY SHEET



(57) Abstract: A process of producing a functionally graded sheet of material (preferably aluminum alloy) that undergoes a transformation from an original property to a transformed property when subjected to energy input. The process comprises irradiating a surface of the sheet article with an energy beam having an energy level and duration effective to modify the original property of the material of the sheet article to provide the material with said transformed property. The energy beam is directed into a plurality of zones forming a pre-determined repetitive pattern over the surface of the sheet article thereby creating a plurality of mutually spatially separated zones of the material provided with the transformed property arranged in the repetitive pattern.

40445 A1

WO 2005/040445 A1



Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

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

-1-

Functionally Graded Aluminum Alloy Sheet

TECHNICAL FIELD

This invention relates to functionally graded materials (FGMs) and, more particularly, the invention relates to a process of producing functionally graded aluminum alloy sheet articles and the sheet articles thereby produced.

BACKGROUND ART

5

10

20

25

It is well known that abrupt transitions in materials composition and properties within a component often result in sharp local concentrations of stress. It is also known that these stress concentrations are greatly reduced if the transition from one material to the other is made gradual. These two considerations form the basic foundation for the concept of functionally graded materials (FGMs). By definition, FGMs are used to produce components featuring engineered gradual transitions in microstructure and/or composition, the presence of which is motivated by functional performance requirements that vary with location within the part. With FGMs, these requirements are met in a manner that optimizes the overall performance of the component. FGMs are a relatively new form of composites having a continuous variation in composition along a certain direction.

In general, FGMs containing a metallic phase can be produced by two principal classes of processes. The first class of processes is called "constructive processes," where the FGM is constructed layer by layer, in a manner that starts with an appropriate distribution of constituents of the FGM, often in a precursor of the components. For example, various powder densification and coating processes are included in this class of FGM process. The powder densification process may include liquid phase sintering, infiltration, reactive powder process, etc. and the coating process may include plasma spray forming, laser cladding, electroforming process, vapor deposition process, lamination process, etc. These processes are attractive because there is essentially no limit on gradients that can be produced. This leaves full flexibility for designers to make the most of the material's macrostructure to achieve the best performance.

The second class of processes, called "transport based processes," relies on natural transport phenomena to create gradients within a component. These "transport based processes" use the flow of fluid, the diffusion of atomic species, or the conduction of heat to create gradients in local microstructures and/or compositions. If these processes are quantitatively understood and harnessed, gradients produced can still be optimized, albeit within a narrower window of possible structures. Both heat and mass diffusion have been used for centuries to create functional, microstructural, and/or compositional gradients in steel. Fluid flow, interfacial segregation, and slow solid state diffusion during solidification are responsible for macro-segregation in single crystals and alloy castings. Although generally viewed as a problem in the processing of homogeneous materials, these are naturally segregative phenomena which can be used to create tailored gradients within a component.

These transport based processes include several industrially important or
promising processes. However, transport processes do not permit pre-selection of
gradient profiles from an unlimited array of possibles, as is afforded in constructive
processes. Further, a quantitative control of the gradient profile is limited by
nature. The spectrum of possible gradients is often wide, but leaving significant
room for gradient optimization in design.

Accordingly, there has been a need to improve or advance the conventional FGM processes and, furthermore, develop a new process for manufacturing a new functionally graded materials, in which the control of gradients can be achieved in a more quantitative and predictable manner in a cost-efficient way, while well-performing as a FGM.

25 DISCLOSURE OF THE INVENTION

5

10

An object of the present invention, at least in one of its forms, is to provide a functionally graded sheet material (preferably aluminum alloy) which has graded microstructures and mechanical properties.

Another object of the present invention, at least in one of its forms, is to provide a process for producing a functionally graded sheet material (preferably

- 3 -

aluminum alloy), where a graded microstructure/mechanical property as required can be achieved in a predictable manner.

According to one aspect of the present invention, there is provided a process of producing a functionally graded sheet article made of material that undergoes a transformation from an original property to a transformed property when subjected to energy input, which process comprises: irradiating a surface of the sheet article with an energy beam having an energy level and duration effective to modify said original property of the material of the sheet article to provide said material with said transformed property, without causing melting of said material, wherein the energy beam is directed into a plurality of zones forming a pre-determined repetitive pattern over the surface of the sheet, thereby creating, within at least one region of said sheet article having said original property, a plurality of mutually spatially separated zones of said material provided with said transformed property arranged in said repetitive pattern.

The invention also relates to a functionally graded sheet article produced according to the above process or a sheet article having the same properties produced in any other way.

More preferably, the invention relates to a process of producing a functionally graded aluminum alloy sheet, which comprises irradiating a surface of an aluminum alloy sheet of predetermined thickness with an energy beam having energy and duration effective to modify an original property of the alloy of the sheet completely throughout said sheet thickness to form an alloy having a modified property, without causing melting of said alloy, wherein the energy beam is directed into a plurality of zones forming a pre-determined repetitive pattern over the surface of the sheet, thereby creating, within at least one region of said alloy sheet having said existing property, a plurality of mutually spatially separated regions of said alloy having said modified property extending through said sheet thickness and arranged in said repetitive pattern.

A further understanding, aspects and advantages of the present invention will be realized by reference to the following description, appended claims and

accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiment(s) of the invention is described in more detail below with reference to the accompanying drawings, in which:

5 Fig. 1 schematically illustrates a functionally graded aluminum alloy sheet in accordance with one preferred embodiment of the present invention; and

Fig. 2 is a cross-sectional view taken along the line A-A in Fig. 1

BEST MODES FOR CARRYING OUT THE INVENTION

In the present invention, at least in the preferred forms, sheet, plate or shaped extrusions (hereinafter referred to collectively as sheet articles) made of a material that undergoes a transformation of properties (an original or existing property is converted to a transformed or modified property) when subjected to an input of energy is treated with an energy beam in a repeating pattern in order to form regions exhibiting one physical property in the treated areas and another physical property in the untreated areas.

While the invention relates to any material that exhibits such a transformation, the invention is normally applied to metal alloys, e.g. alloys of Ti and Al, and most preferably to aluminum alloys. In this way, aluminum alloys may be treated so that certain properties (functional characteristics) vary across the material's surface and to some extent into its depth (preferably completely through the thickness of the article). The invention is a departure from most prior art processes, which aim to achieve a surface having homogeneous properties with a variation through the thickness of the material. Moreover, the invention provides variable properties arranged in a matrix-like fashion (repetitive pattern) in the planar direction throughout a semi-fabricated material. In the case of automotive sheet, for example, if small age-hardened regions are separated by areas of unhardened metal, then a better combination of strength, ductility and toughness is possible.

- 5 -

The energy beam used to introduce energy into localized areas of the material may be a beam that introduces heat, e.g. a laser beam, or a beam that introduces mechanical energy with or without heat, e.g. water jet or ultrasonic beam.

For example, a pulsed laser array, may be used to impart solutionizing / age hardening to local areas only of a sheet article.

5

10

15

Typically sheet is processed to provide an homogeneous distribution of microstructure and properties in the plane of the sheet, which is desirable for marny applications. A good example is age-hardened sheet, where high strength is obtained with sacrifice of ductility and toughness. If the age-hardened regions are isolated from each other, a higher level of toughness can be obtained. By producing sheet with spatially graded properties a better combination of strength, ductility and toughness can therefore be obtained.

The details of the repetitive pattern, e.g. whether the pattern is regular or irregular, what are the sizes of the zones and their spacing, what is the shape of the zones (e.g. circular, other shape or irregular), what is the minimum number of zones per unit area, etc., depends on the nature of the alloy or other material and the physical characteristics that are intended to be produced.

As shown in the attached figures, in a preferred form the present invention may be used to create a distribution of zones 14 in a sheet article 10 that have the 20 enhanced properties, while the zones are spatially distributed so that regions 12 with other properties separate them. The zones 14 in this example are generally circular with a diameter S and a spacing of D1 in the transverse direction and a spacing D2 in the longitudinal direction of the sheet. D1 and D2 may be the same or different. As an example, the zones 14 may be regions that are precipitation 25 hardened and may be separated by an unhardened matrix. As a result, cracks nucleated in the hardened zones are "blunted" when they impinge on the more ductile surrounding matrix. These zones can be created in a variety of ways. For example, in the case of precipitation hardened zones, solution treated sheet may be subjected to an array of short thermal spikes from a pulsed laser array. The 30 lasers provide the thermal energy necessary to produce precipitation in the zones

5

subjected to the laser beam. The thermal spike can be enhanced by laying a preliminary pattern of "ink" on the sheet which will reduce the laser reflectivity if necessary. Alternatively, the initial sheet may be in an age-hardened condition and the laser used to provide zones of local solutionizing. This results in soft islands in a hard matrix.

Other methods can also be employed for providing hardened zones, such as pulsed ion implantation. In this case, the local chemistry is changed to provide the enhanced strength.

A key feature is to provide a spatial distribution of properties in the plane of the sheet article.

A preferred feature of the present invention is that an energy beam is used at an energy level capable of modifying the properties of an alloy sheet article completely through the thickness of the article from one planar surface to the other. This can be done without melting the alloy, even at the surface being 15 treated. The modified surface characteristics are therefore not just provided at the surface of the article but extend through the body of the sheet. This is not always essential, however, as in many cases there is no need to change the characteristics fully through the thickness of the material. For example, fracturing is often a surface-initiated phenomenon. Nevertheless, if treatment completely through the thickness of the material is required, the power of the energy system 20 will have to penetrate to that depth, preferably without causing any melting of the material at the surface or in the interior (although there is often a large temperature gap between the temperature at which the transformation occurs and the melting temperature of the material, so melting is not usually a significant problem). Depending on the energy beam employed, there will therefore be a 25 limitation on the thickness that can be treated.

Functionally graded material are under development, but these are designed to provide a range of properties through the thickness, such as high wear resistance at the surface. One objective of the present invention, at least in preferred forms,

-7-

is to provide uniform bulk properties but making use of a spatially graded microstructure which provides locally variable properties.

5

10

15

20

25

The invention is particularly suitable for producing strength-to ughness combinations as noted above, but it may also be used to produce combinations of other micro-structural features. For example, local regions of different crystallographic texture.

The inventors of the present application have coined the term "In-Plane Spatially Graded (IPSG) materials" for this type of product. The term envisages property variations in the plane of the sheet by spatially varying the microstructure. This spatial variation in microstructure can potentially be created in several different ways. Pulsed lasers are now available with pulses of 1 – 1000 microJ, while irradiating an area of 400nm - 50μm, so that the associated energy can be used to modify the microstructure on this spatial scale. High-resolution scanning lasers are also now available, and the thermal treatment can also be produce be an electron beam which can also generate a fine beam diameter. Alternatively, micro-water jet technology has been developed to produce jets of tens of microns in diameter, and these may be used to mechanically impinge on a sheet surface and hence produce variable levels of cold work. Depending on the method used to modify the microstructure, a spatial distribution of essentially circular areas, or a grid pattern can be generated in the sheet within which the microstructure is modified. However, there is no need to limit the pattern to circular areas and a regular pattern. This depends on the level of properties required and also on the particular material employed. The treated zones are preferably evenly distributed in the planar direction of the material. A close-packed arrangement is generally the best (e.g. if a unit area of the pattern is a square, treated zones would be provided at each of the corners with a further treated zone in the center of the square). In some cases, there may be an advantage to making the spacing of the treated areas different in the longitudinal and transverse directions, for example if loading of a sheet article is likely to be loaded differently in different directions.

-8-

Several techniques may be use for the purpose of producing a spatially modified microstructure of hard and soft regions that improves the strength – fracture strain combination of the sheet, as indicated in the following.

5

10

15

20

25

30

- (1) Sheet/extrusion in the T4 type temper is subjected to spatially distributed thermal spikes to produce higher strength precipitation hardened regions. The temperature/time cycles required to do this depend on the particular alloy involved, but temperatures in the 150°C to 250°C range is required for AA6000 series alloys, and the duration will be a function of the level of hardening required. Potentially, age hardening can more than double the strength of the regions thermally spiked, but this would probably require pulse durations of the order of a second at the highest temperatures. However, significant hardening can be achieved with much shorter pulse times. The durations required to achieve a particular strength level can be obtained from conventional age hardening curves. This approach produces regions of hard material surrounded by a general matrix that is softer and more ductile.
 - (2) Sheet/extrusion that is in the age-hard ened temper is subjected to spatially distribute thermal spikes to produce regions that are locally solutionised and hence softer. In this case the temperatures required are higher, while the duration times will be much shorter. For AA6000 series alloys, solutionising occurs above 500°C, while for AA7000 series alloys, it will occur above 450°C. At 520°C, both types of alloys would be solutionised without any need for a significant hold time. This approach results in "soft" regions surrounded by a matrix of precipitation hardened alloy.
 - (3) Another way of producing a spatial distribution of hard and soft regions in a sheet is to begin with a strain hardened sheet and use a thermal spike to locally anneal spatially distributed regions of the sheet. This approach is specifically useful in the non-heat treatable AA1000, 3000 and 5000 series alloys. The temperature necessary to produce softening depends on the level of cold work and the degree of softening required, but softening will

5

typically begin at about 250°C, so thermal excursions above this temperature produce various extents of softening. This approach results in "soft regions" in a strain-hardened matrix.

(4) The reverse of situation (3) can be achieved by locally working spatially distributed regions of an annealed sheet, with the local level of hardening depending on the degree of cold work. Mechanical or other means of impingement may be used to achieve the local working. This approach perturbs the profile of the sheet, which limits its use somewhat.

Finally, it is conceivable that, in the future, sheet and extrusions with highly

metastable structures, such as amorphous or nanophase material, will be
available. To fully utilize such material, a FGM or IPSG approach would be
advantageous to produce a compromise in properties. For example, the
susceptibility of amorphous material to flow localization, and the low tensile
ductility exhibited by nanophase material could be alleviated by producing the

duplex microstructures associated with IPSG. In the case of amorphous material,
a thermal spike would produce local crystallized regions that would inhibit flow
localization. With nanophase material, a thermal spike will locally coarsen the
microstructure which increases the ductility.

While the present invention has been described with reference to several preferred embodiments, the description is illustrative of the invention and is not to be construed as limiting the invention. Various modifications and variations may occur to those skilled in the art, without departing from the scope of the following claims.

CLAIMS:

- A process of producing a functionally graded sheet of material that undergoes a transformation from an original property to a transformed property when subjected to energy input, which process comprises: irradiating a surface of the sheet article with an energy beam having an energy level and duration effective to modify said original property of the material of the sheet article to provide said material with said transformed property, without causing melting of said material, wherein the energy beam is directed into a plurality of zones forming a pre-determined repetitive pattern over the surface of the sheet, thereby creating,
 within at least one region of said sheet article having said original property, a plurality of mutually spatially separated zones of said material provided with said transformed property arranged in said repetitive pattern.
 - 2. The process of claim 1, carried out on a sheet article made of a metal alloy.
- 15 3. The process of claim 1, carried out on a sheet article made of an aluminum alloy.
 - 4. The process of claim 1, wherein said energy level of said energy beam is sufficient to cause said convert said original property to said transformed property through the entire thickness of the sheet article in said plurality of zones.
- 5. The process of claim 1, wherein the original property of the material is that the material is in a solutionized condition, and wherein said energy beam is used to modify the material to produce an age-hardened condition as said transformed property.
- 6. The process of claim 1, wherein the original property of the material is that the material is in an age-hardened condition, and wherein said energy beam is used to modify the material to produce a solutionized condition as said transformed property.

- 11 -

- 7. The process of claim 1, wherein the original property of the sheet is that the sheet is in a work-hardened condition, and wherein said energy beam is used to modify the material to produce a transformed property selected from the group consisting of recovered, recrystallized and annealed.
- 5 8. The process of claim 1, wherein the original property of the material is that the material is in a condition selected from the group consisting of recovered, recrystallized and annealed, and wherein the energy beam is used to modify the material to produce a work-hardened condition as said transformed property.
- 10 9. The process of claim 1, wherein the original property of the material is that the material is in an unhardened condition, and wherein the energy beam is used to implant ions in the sheet to produce hardening as said transformed condition.
- 10. The process of claim 1, wherein the energy beam is selected from15 the group consisting of a laser beam, an electron beam and an ion beam.
 - 11. The process of claim 1, wherein the energy beam is a water jet.
- 12. A functionally graded sheet article made of a material that undergoes a transformation from an original property to a transformed property when subjected to energy input, said sheet article having been produced by a process
 20 according to claim 1.
 - 13. The functionally graded sheet article of claim 12, wherein said material is an aluminum alloy.
- 14. A functionally graded aluminum alloy sheet article, comprising a material having a surface provided with a plurality of spatially separated zones
 25 forming a pre-determined repetitive pattern within said surface, wherein the material within said zones has a property different from the material in said remainder of said material.

- 12 -

- 15. The sheet article of claim 14, wherein said zones having said property different from said remainder of said material extend completely through said sheet article.
- The sheet article of claim 14, wherein said material is an aluminumalloy.
 - 17. The sheet article according to claim 14, wherein said zones are approximately circular with a diameter in the range of 400 nm to 50 microns.
 - 18. The sheet article according to claim 16, wherein the alloy in said zones is age-hardened and the alloy in said remainder is solutionized.

1/1

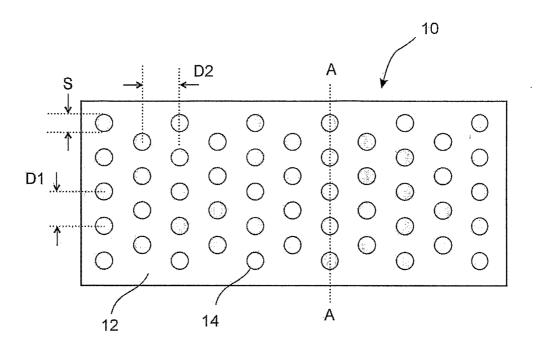


Fig. 1

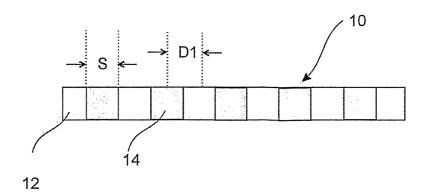


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.

A. CLASSIFICATION OF SUBJECT MATTER C22F-03/00

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22F-03/00; C22F-01/00; C22F-1/04; C22C-21/00; C22C-33/04; B01J-19/08;

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms QUESTEL-ORBIT; DELPHION (incl. Derwent); ESPACENET; STN (Caplus; Compendex; Metadex; Aluminium);

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Citation of document, with indication, where appropriate, of the relevant	Relevant to claim No(s).
Danilenco V.E. "Distinctive features of the surface microrelief of technical iron in the zone of pulse radiation", Metal Science and Heat Treatment (Russia), (2001), 43, (1-2), 58-60 abstract.	1-4, 10, 12-18
DD 246569 (KEITEL, S. et al.) 10 June, 1987 abstract.	1-18
DD 242429 (FINN T. et al.) 28 January, 1987 abstract.	1-18
•	Danilenco V.E. "Distinctive features of the surface microrelief of technical iron in the zone of pulse radiation", Metal Science and Heat Treatment (Russia), (2001), 43, (1-2), 58-60 abstract. DD 246569 (KEITEL, S. et al.) 10 June, 1987 abstract. DD 242429 (FINN T. et al.) 28 January, 1987

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

*	Special categories of cited documents: "T"
"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 doubt on priority claim(s) or which is cited to establish the publication date of another citation or other "Y" special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other

document published prior to the international filing date but later than the priority date claimed

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 document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is staken alone 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	Date of mailing of the international search report 04 March 2005 (04-03-2005)			
22 February 2005 (22-02-2005)				
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	Authorized officer Michael M. Morgovsky (819) 953-0765			

Facsimile No: 001(819)953-2476

INTERNATIONAL SEARCH REPORT

International application No. PCT/CA2004/001877

		PCT/CA2004/001877
C (Continua	ation). DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the rele	evant Relevant to claim No(s).
Y	Nicolas G. "Surface properties modification obtained on cerami metals resulting from excimer laser processing technic Proceedings of SPIE-The International Society for Optical Enginee (1998), 3343 (Pt. 2, High-Power Laser Ablation), 1023-1031.	Įue",
**	abstract.	
Y	EP 237448 (LASLAZ, G) 16 December, 1987 abstract; claims 1-5, 11;	1-3
Α	assaus, same 1 s, 11,	1-18
	Romano V. et al. "Laser surface microstructuring to improve tribological systems", Proceedings of SPIE-The International Socion Coptical Engineering (2003), 5121 (Laser Processing of Advantage Materials and Laser Microtechnologies), 199-211.	•
	the whole document	
		·
	·	
		`
	·	
~	210 (continuation of second sheet) (Junear 2004)	

INTERNATIONAL SEARCH REPORT

International application No. PCT/CA2004/001877

Information on patent family members

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
DD 246569		NONE	
DD 242429		NONE	
EP237448		AT43364T T CA1275762 C	15-06-1989 06-11-1990
		DE3760178D D1 EP0237448 A1	29-06-1989 16-09-1987
		FR2594852 A1 GR3000014T T3	28-08-1987 31-10-1989
		JP62290883 A US4750945 A	17-12-1987 14-06-1988