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(54) **SURFACE TREATED SHAPE MEMORY MATERIALS AND METHODS FOR MAKING SAME**

OBERFLÄCHENBEHANDELTE FORMSPEICHERMATERIALIEN UND HERSTELLUNGSVERFAHREN DAFÜR

MATERIAUX A MEMOIRE DE FORME TRAITES EN SURFACE ET PROCEDE DE PRODUCTION ASSOCIES

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Description

BACKGROUND OF THE INVENTION

[0001] Shape memory materials such as nickel titanium (NiTi) alloys are promising materials for surgical implants in orthopedics due to their unique shape memory effect (SME) and super-elasticity (SE) that other common orthopedic materials such as stainless steels and titanium alloys do not possess. Their mechanical properties are also closer to that of cortical bones than stainless steels and titanium alloys. The materials display superior wear resistance to CoCrMo alloys used in bone trauma fixation. Several other favorable properties of the materials have also been investigated, and good bio-compatibility has also been reported. However, some negative effects have also been pointed out. For example, Berger-Gorbet et al. have found that the osteogenesis process and osteonectin synthesis activity in NiTi alloys are unfavorable compared to stainless steels and titanium alloys.[1] Jia et al. in their study revealed that the cell death rate was severe on NiTi alloys.[2]

[0002] These problems are believed to stem from the poor corrosion resistance of the materials, which may lead to an increase in their cytotoxicity. It is most likely that some toxic components released from the substrate cause the cell death rather than the apoptosis.[3] Shih et al. reported that the supernatant and corrosive products from NiTi may result in the death of smooth muscle cells, especially when the amount of released nickel is higher than 9 ppm.[4] A few other studies have also reported that nickel ions [5,6] leached from the alloys cause allergic reactions in nickel hypersensitive patients.[7-10] While the homogeneity of the materials microstructures and the surface morphology may alter the anti-corrosion ability of NiTi alloys, there is no doubt that the corrosion resistance and anti-wear properties of the materials must be enhanced before the materials can be widely used clinically, especially as orthopedic implants with couplings where fretting is expected.

[0003] Titanium carbides and nitrides have excellent mechanical and chemical properties, for example, good wear resistance, inactive with numbers of chemical substances and outstanding hardness [11-16]. Titanium oxides are known to be fairy compatible with living tissues [17-20]. They are also inactive to many chemical reactions. In surface coating industries, these elements have been applied to improve the mechanical and corrosion properties of the substrates through various methods [21-25] for a period of time.

SUMMARY OF THE INVENTION

[0004] The invention provides a method for the altering surface composition of a nickel titanium alloy part to increase biocompatibility, comprising implanting nitrogen or oxygen on the surface of the nickel titanium alloy part by plasma immersion ion implantation and deposition or related ion-beam and plasma-based techniques such as plasma-enhanced vapor phase deposition (PECVD), physical vapor deposition (VPD), and chemical vapor deposition (CVD), wherein the energy of the incident specimen used for surface treatment of the material ranges from 500 eV to 100 keV for plasma immersion ion implantation and deposition.

[0005] The invention also provides orthopedic, vascular, and esophageal implants made from the foregoing materials.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006]

FIG. 1 is a plot of Ni depth profiles acquired from the nitrogen, acetylene and oxygen PIII surface treated samples and control.

FIG. 2 includes photomicrographs of treated and untreated NiTi (control) after two days of cell culturing showing the EGFP expressing mouse osteoblasts. (A) NiTi alloy without surface treatment, (B) with nitrogen PIII implantation, (C) with acetylene PIII implantation, and (D) with oxygen PIII implantation.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

[0007] Shape memory materials such as nickel titanium alloys (NiTi) are useful materials in biomedical applications due to their unique properties. However, for prolonged use in a human body, deterioration of the corrosion resistance of the materials becomes a critical issue, because of the possibility of deleterious ions released from the substrate to living tissues. Therefore, we suggested the use of plasma immersion ion implantation and deposition and related ion-beam and plasma-based techniques to implant some other elements, such as C_2H_2, N_2, and O_2, into NiTi substrates to alter corrosion resistance and wear properties of the alloys. We have successfully demonstrated that the corrosion resistance and wear properties of nickel titanium shape memory alloys can be enhanced by implanting nitrogen, carbon and oxygen onto the substrate surface. Additionally, with the use of plasma immersion ion implantation or deposition,

the biological properties such as osteoconductivity and hydrophilicity can also be reduced or enhanced.

[0008] The invention provides a method for the altering surface composition of a nickel titanium alloy part to increase biocompatibility, comprising implanting nitrogen or oxygen on the surface of the nickel titanium alloy part by plasma immersion ion implantation and deposition, wherein the energy of the incident specimen used for surface treatment ranges from 500 eV to 100 keV for plasma immersion ion implantation and deposition. The nickel titanium alloy is preferably a shape memory alloy, and has a nickel content ranging from about 20-80% of nickel and 80-20% of titanium. The surface implantation of elements enhances the mechanical properties of the alloy, such as hydrophilicity, corrosion and wear resistance. The nickel titanium alloy part can be reduced or enhanced. In practicing the invention, the plasma immersion ion implantation and deposition or related ion-beam and plasma-based techniques such as plasma-enhanced vapor phase deposition (PECVD), physical vapor deposition (VPD), and chemical vapor deposition (CVD) can reduce, terminate or prevent the deleterious ions from being released from the substrate of the shape memory materials. The materials may be biomaterials used for orthopedics, urologics, vascular surgery, hepatobiliary surgery or esophageal surgery. The energy of the incident species used for surface treatment of the materials ranges from 500 eV to 100 keV for implantation and deposition. Preferably, the energy of the surface treatment of the materials ranges from 500 eV to 1000eV for implantation and deposition. The direct current is applied with the parameters 0 Hz repetition with 'infinite' pulse duration to 5000 Hz. The material implanted is a nitrogen source, a carbon source, or an oxygen source, gaseous, liquid, or solid form. The nitrogen source is nitrogen gas. The carbon source is acetylene or a derivative thereof. The oxygen source is oxygen gas.

[0009] The method may be used to make an orthopedic, vascular, or esophageal implant.

[0010] For the purposes of promoting an understanding of the principles of the plasma immersion ion implantation and deposition or related ion-beam and plasma-based techniques such as plasma-enhanced vapor phase deposition (PECVD), physical vapor deposition (VPD), and chemical vapor deposition (CVD) on the surface of shape memory materials such as Ti - 50.8% at Ni alloy, the specific preferred embodiments of the invention will be described.

[0011] Figure 1 indicates the Ni concentration profiles of the samples with and without PIII surface treatment. The Ni concentrations in the implanted region in nitrogen, acetylene and oxygen plasma-implanted samples are much lower when compared to the non-coated control sample. Nitrogen PIII gives rise to the highest Ni suppression compared to oxygen PIII.

[0012] The treatment methods for acetylene, nitrogen and oxygen implantation the sample were ground, polished to a shiny surface texture, and then ultrasonically cleaned with acetone and ethanol before deposition or implantation was conducted in the plasma immersion ion implanter. The deposition and implantation parameters of acetylene, nitrogen and oxygen implantation samples were displayed in Table 1. The elemental depth profiles as shown in Figure 1 were determined by X-ray photoelectron spectroscopy (XPS) (Physical Electronics PHI 5802, Minnesota, USA).

Table 1 -- Treatment parameters of plasma immersion ion implantation and deposition

Sample	NiTi with acetylene implantation	NiTi with nitrogen implantation	NiTi with oxygen implantation
Gas type	C_2H_2	N_2	O_2
RF	-	1000W	1000W
High voltage	-40kV	-40kV	-40kV
Pulse width	30μs	50μs	50μs
Frequency	200Hz	200Hz	200Hz
Duration of implantation (min)	90	240	240
Base pressure	$1x10^{-5}$Torr	$7.0x10^{-6}$Torr	$7.0x10^{-6}$Torr
Working pressure	$2.0x10^{-3}$Torr	$6.4x10^{-4}$Torr	$6.4x10^{-4}$Torr
Dose	$5.5x10^{16}cm^{-2}$	$9.6x10^{16}cm^{-2}$	$1.0x10^{17}cm^{-2}$
Annealing pressure	$1.0x10^{-5}$Torr	$8.0x10^{-6}$Torr	$8.0x10^{-6}$Torr
Annealing temperature (°C)	600	450	450
Duration of annealing (h)	5	5	5

Nano-indentation tests (MTS Nano Indenter XP, USA) were conducted on five areas to determine the average hardness and Young's modulus of the treated and control samples. The hardness of the control sample is 4.5GPa and the Young's modulus is 57GPa.

[0013] Table 2 lists the results of the hardness (H) and Young's modulus (E) of the untreated control and treated samples surfaces using nano-indentation test.

Table 2 -- Young's modulus and hardness of control and the treated samples surfaces

Sample	NiTi	NiTi implanted with acetylene	NiTi implanted with nitrogen	NiTi implanted with oxygen
Young's modulus (GPa)	57	110 - 70	150 - 65	115 - 60
Hardness (GPa)	4.5	9.5 - 4.5	11 - 5	8 - 4

All the surface-treated samples possess higher surface hardness and Young's modulus than those of the control. It implies that the treated surfaces are mechanically stronger than the NiTi substrates underneath and can withstand mechanical shock more effectively. Among the treated surfaces, the nitrogen-implanted layer has the largest. H and E, followed by the acetylene- and oxygen-implanted layers.

[0014] Table 3 lists the amounts of Ni leached from the surface-treated and untreated samples after the electrochemical tests as determined by inductively coupled plasma mass spectrometry (ICPMS). Electrochemical tests based on ASTM G5-94 (1999) and G61-86 (1998) were performed by a potentiostat (VersaStat II EG&G, USA) using a standard simulated body fluid (SBF) at a pH of 7.42 and temperature of 3770.5 1 C (37.5°C). The ion concentrations in the SBF are shown in Table 4. A cyclic potential spanning between -400 and +1600mV was applied at a scanning rate of 600 mV/h. Before the electrochemical tests, the medium was purged with nitrogen for 1 h to remove dissolved oxygen and nitrogen purging continued throughout the measurements. The SBF taken from each sample after the corrosion test was analyzed for Ni and Ti employing inductively coupled plasma mass spectrometry (ICPMS) (Perkin Elmer, PE SCIEX ELAN6100, USA). The amounts of Ni leached from all treated samples were significantly reduced. The magnitudes were only about 0.03 to 0.04% of that of the control samples. The ion concentrations in the SBF are shown in Table 4.

Table 3 -- Amounts of Ni and Ti ions detected in SBF by ICPMS after electrochemical tests

Sample	Ni content (ppm)	Ti content (ppm)
	Ni	Ti
Control	30.2324	0.1575
C-treated	0.0082	0.057
N-treated	0.0117	0.0527
O-treated	0.0123	0.002

Table 4 -- Ion concentration of SBF solution

	Concentration (mM)							
	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	HPO_4^{2-}	SO_4^{2-}
SBF	142.0	5.0	2.5	1.5	4.2	148.5	1.0	0.5

[0015] Figure 2 demonstrates that the nitrogen, acetylene and oxygen plasma-implanted samples are well tolerated by the EGFP-expressing osteoblasts. The osteoblasts were isolated from calvarial bones of 2-day-old mice that ubiquitously express an enhanced green fluorescent protein (EGFP) were used to culture in a Dulbecco's Modified Eagle Medium (DMEM) (Invitrogen) supplemented with 10% (v/v) fetal bovine serum (Biowest, France), antibiotics (100 U/ml of penicillin and 100 μg/ml of streptomycin), and 2mM L-glutamine at 37°C in an atmosphere of 5% CO_2 and 95% air. The specimens (1 mm thick and 5 mm in diameter) were fixed onto the bottom of a 24-well tissue culture plate (Falcon) using 1% (w/v) agarose. A cell suspension of 5,000 cells was seeded onto the surface of the untreated NiTi samples and the three types of plasma-implanted samples (oxygen, nitrogen, and acetylene). Cells were grown in one ml of medium and changed every two days. Cell attachment and proliferation were examined after the second day of culture. After culturing for two days, the cells started to attach to and proliferate on all the samples. Our results unequivocally demonstrate that there is no immediate cytotoxic effect on all of the surface treated samples.

[0016] It should be apparent to a person of ordinary skill that the improved alloys obtainable with the present invention can be used for a wide variety of applications, both as biomaterials and for other applications where such alloys might prove advantageous. For example, the alloys may be used to fashion orthopedic implants including replacement joints such as hips, knees, shoulders, elbows, fingers, or for rods, screws, nails, spinal implants and the like used for orthopedic purposes. They may also be used to form thin matches useful for making patches, tubing, and devices useful in urologic, cardiac, spinal, cerebrospinal, gastrointestinal, hepatobiliary, vascular, or esophageal surgery.

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Claims

1. A method for the altering surface composition of a nickel titanium alloy part to increase biocompatibility, comprising implanting nitrogen or oxygen on the surface of the nickel titanium alloy part by plasma immersion ion implantation and deposition,
wherein the energy of the incident species used for surface treatment of the materials ranges from 500 eV to 100 keV for plasma immersion ion implantation and deposition.

2. The method according to claim 1, wherein the nickel titanium alloy is a shape memory alloy, and has a nickel content ranging from 20-80% of nickel and 80-20% of titanium.

3. A method according to claim 1, wherein the surface implantation of elements enhances the mechanical properties of the alloy.

4. A method according to claim 3, wherein the surface mechanical properties include hydrophilicity, corrosion and wear resistance.

5. A method according to claim 2, wherein the bioactivity of the nickel titanium alloy is reduced or enhanced.

6. A method according to claim 2, wherein the plasma immersion ion implantation and deposition or related ion-beam and plasma-based techniques such as plasma-enhanced vapour phase deposition (PECVD), physical vapour deposition (VPD), and chemical vapour deposition (CVD) reduce the Ni ions released from the substrate of the shape memory materials.

7. A method according to claim 2, wherein the materials are biomaterials used for orthopedics, urologics, vascular surgery, hepatobiliary surgery or esophageal surgery.

8. A method according to claim 6, wherein the energy of the incident species used for surface treatment of the materials ranges from 500 eV to 1000 eV for implantation and deposition.

9. A method according to claim 6, wherein direct current is applied with the parameters 0 Hz repetition with infinite pulse duration to 5000 Hz.

10. A method in accordance with claim 2, wherein the material implanted is a nitrogen source or an oxygen source.

11. A method in accordance with claim 10, wherein the nitrogen source is nitrogen gas.

12. A method in accordance with claim 10, wherein the oxygen source is oxygen gas.

13. An orthopaedic implant made in accordance with the method of claim 1.

14. A vascular implant made in accordance with the method of claim 1.

15. An esophageal implant made in accordance with the method of claim 1.

16. A method according to claim 9, wherein the elements are in gas form liquid form, solid form, or composition thereof.

Patentansprüche

1. Verfahren zum Ändern der Oberflächenzusammensetzung eines Nickel-Titan-Legierungsteils zum Erhöhen der Biokompatibilität mit dem Schritt des Implantierens von Stickstoff oder Sauerstoff auf der Oberfläche des Nickel-Titan-Legierungsteils durch Plasmaimmersions-Ionenimplantation und -deposition, wobei die Energie der einfallenden Spezies, welche zur Oberflächenbehandlung der Materialien verwendet wird, im Bereich von 500 eV bis 1000 keV für die Plasmaimmersions-Ionenimplantation und -deposition liegt.

2. Verfahren nach Anspruch 1, wobei die Nickel-Titan-Legierung eine Formgedächtnislegierung ist und einen Nickelgehalt im Bereich von 20-80 % an Nickel und 80-20 % von Titan aufweist.

3. Verfahren nach Anspruch 1, wobei die Oberflächenimplantation der Elemente die mechanischen Eigenschaften der Legierung verbessert.

4. Verfahren nach Anspruch 3, wobei die mechanischen Oberflächeneigenschaften Hydrophilie, Korrosions- und Verschleißwiderstand beinhalten.

5. Verfahren nach Anspruch 2, wobei die Bioaktivität der Nickel-Titan-Legierung reduziert oder erhöht wird.

6. Verfahren nach Anspruch 2, wobei die Plasmaimmersions-Ionenimplantation und - deposition oder verwandte Ionenstrahl- und plasmabasierte Techniken, wie zum Beispiel plasmaverstärkte Dampfphasenabscheidung (PECVD), physikalische Dampfphasenabscheidungen (VPD) und chemische Dampfhasenabscheidungen (CVD) die Nickelionen reduzieren, welche von der Oberfläche der Formgedächtnismaterialien gelöst werden.

7. Verfahren nach Anspruch 2, wobei die Materialien Biomaterialien sind, welche für Orthopädie, Urologie, Gefäßchirugie, Hepatobiliär-Chriugie oder für Ösophageal-Chirugie verwendet werden.

8. Verfahren nach Anspruch 6, wobei die Energie der einfallenden Spezies, welche für die Oberflächenbehandlung der Materialien verwendet wird im Bereich von 500 eV bis 1.000 eV für die Implantation und Abscheidung liegt.

9. Verfahren nach Anspruch 6, wobei ein Gleichstrom mit den Parametern 0 Hz Wiederholungsrate mit einer unbegrenzten Pulsdauer bis zu 5000 Hz angelegt wird.

10. Verfahren nach Anspruch 2, wobei das implantierte Material eine Stickstoffquelle oder eine Sauerstoffquelle ist.

11. Verfahren nach Anspruch 10, wobei die Stickstoffquelle Stickstoffgas ist.

12. Verfahren nach Anspruch 10, wobei die Sauerstoffquelle Sauerstoffgas ist.

13. Orthopädisches Implantat hergestellt in Übereinstimmung mit dem Verfahren nach Anspruch 1.

14. Gefäßimplantat hergestellt nach dem Verfahren gemäß Anspruch 1.

15. Ösophageales Implantat hergestellt nach dem Verfahren gemäß Anspruch 1.

16. Verfahren nach Anspruch 9, wobei die Elemente in Gasform, Flüssigform, Festform oder einer Zusammensetzung davon sind.

Revendications

1. Procédé pour la composition de surface changeante d'un élément d'alliage de nickel titane pour augmenter la biocompatibilité, comprenant l'implantation d'azote ou d'oxygène sur la surface de l'élément d'alliage de nickel titane par implantation et dépôt d'ions par immersion dans un plasma,
dans lequel l'énergie de l'espèce incidente utilisée pour le traitement de surface des matières s'étend de 500 eV à 100 keV pour l'implantation et le dépôt d'ions par immersion dans un plasma.

2. Procédé selon la revendication 1, dans lequel l'alliage de nickel titane est un alliage à mémoire de forme, et a une teneur en nickel allant de 20 à 80 % de nickel et de 80 à 20 % de titane.

3. Procédé selon la revendication 1, dans lequel l'implantation de surface d'éléments améliore les propriétés mécaniques de l'alliage.

4. Procédé selon la revendication 3, dans lequel les propriétés mécaniques de surface incluent le caractère hydrophile, la résistance à la corrosion et à l'usure.

5. Procédé selon la revendication 2, dans lequel la bioactivité de l'alliage de nickel titane est réduite ou améliorée.

6. Procédé selon la revendication 2, dans lequel l'implantation et le dépôt d'ions par immersion dans un plasma ou

des techniques liées à base de plasma et de faisceau d'ions comme le dépôt en phase vapeur amélioré au plasma (PECVD), le dépôt physique en phase vapeur (VPD) et le dépôt chimique en phase vapeur (CVD) réduisent les ions Ni libérés provenant du substrat des matières à mémoire de forme.

7. Procédé selon la revendication 2, dans lequel les matières sont des biomatériaux utilisés pour l'orthopédie, l'urologie, la chirurgie vasculaire, la chirurgie hépatobiliaire ou la chirurgie oesophagienne.

8. Procédé selon la revendication 6, dans lequel l'énergie de l'espèce incidente utilisée pour le traitement de surface des matières s'étend de 500 eV à 1 000 eV pour l'implantation et le dépôt.

9. Procédé selon la revendication 6, dans lequel un courant continu est appliqué avec les paramètres de répétition de 0 Hz avec une durée d'impulsion infinie à 5 000 Hz.

10. Procédé selon la revendication 2, dans lequel la matière implantée est une source d'azote ou une source d'oxygène.

11. Procédé selon la revendication 10, dans lequel la source d'azote est un gaz d'azote.

12. Procédé selon la revendication 10, dans lequel la source d'oxygène est un gaz d'oxygène.

13. Implant orthopédique réalisé selon le procédé de la revendication 1.

14. Implant vasculaire réalisé selon le procédé de la revendication 1.

15. Implant oesophagien réalisé selon le procédé de la revendication 1.

16. Procédé selon la revendication 9, dans lequel les éléments sont sous forme de gaz, sous forme de liquide, sous forme de solide, ou une composition de ceux-ci.

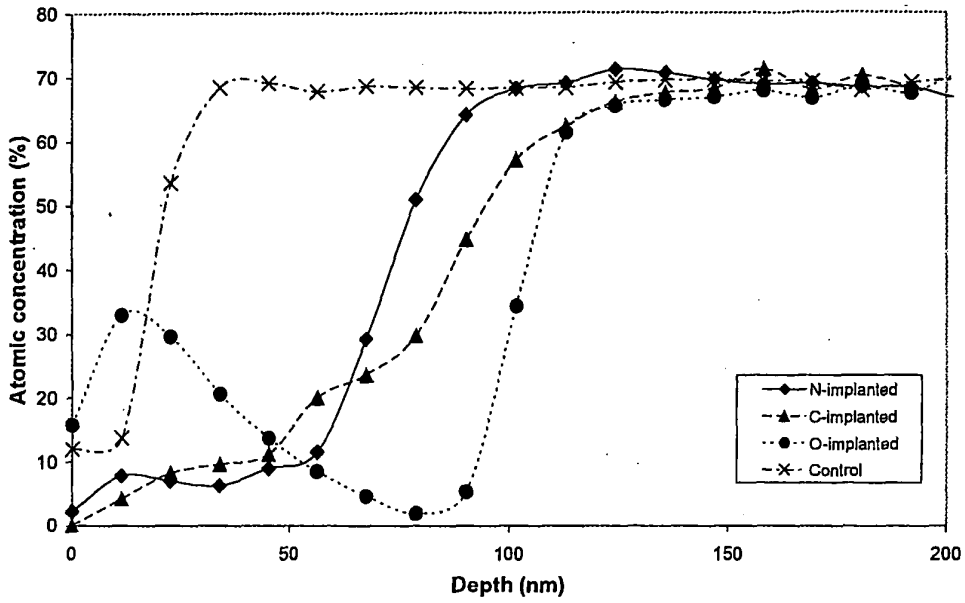
Atomic concentration (%)
Depth (nm)
0
10
20
30
40
50
60
70
80
0
50
100
150
200
N-implanted
C-implanted
O-implanted
Control

FIG. 1

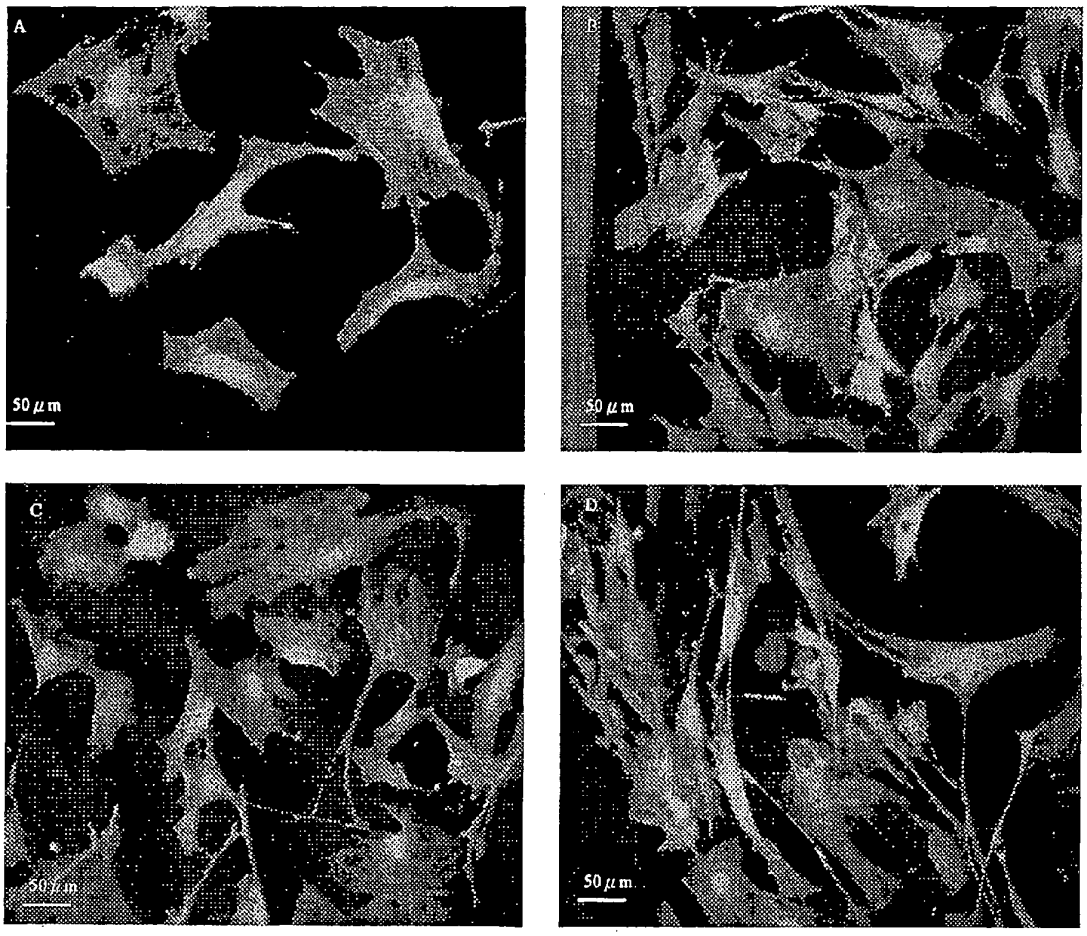

FIG. 2

REFERENCES CITED IN THE DESCRIPTION

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