

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 801 138 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
15.10.1997 Bulletin 1997/42

(51) Int. Cl.⁶: **C22C 1/03**

(21) Application number: **97105999.3**

(22) Date of filing: **11.04.1997**

(84) Designated Contracting States:
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE**
Designated Extension States:
AL LT LV SI

(30) Priority: **12.04.1996 US 631244**

(71) Applicant: **Reading Alloys, Inc.
Robeson, PA 19551 (US)**

(72) Inventors:
• **Higgins, Brian J.
Reading, Pennsylvania 19606 (US)**
• **Kahl, James D.
Robeson, Pennsylvania 19551 (US)**

(74) Representative: **Leonhard, Frank Reimund, Dipl.-
Ing. et al
Leonhard - Olgemöller - Fricke
Patentanwälte
Josephspitalstrasse 7
80331 München (DE)**

(54) Producing titanium-molybdenum master alloys

(57) This invention provides a method for producing substantially homogeneous alloy compositions which contain substantially lower melting base metals, such as titanium, and large amounts of refractory metals, such as molybdenum, tantalum, niobium, tungsten. The invention further provides a method for producing titanium base binary master alloys containing substantial

amounts of molybdenum, preferably containing about 50% molybdenum with the balance being titanium, which are substantially free of molybdenum inclusions and thus are acceptable for subsequent alloying into final titanium base alloys.



FIG. 1

EP 0 801 138 A2

Description

The invention relates to titanium base alloys, and more particularly to titanium base binary master alloys containing substantial amounts of refractory metals, such as molybdenum, which are suitable for further alloying into titanium base alloys. This invention also relates to methods for producing alloys containing substantial amounts of refractory metals, such as high molybdenum (and other refractory)-containing titanium base master alloys.

Titanium metal and titanium base alloys are low weight, yet relatively strong metals, with high heat and corrosion resistance. These metals are in great demand today as preferred materials for use in aircraft, space shuttle, and military applications.

In the production of titanium base alloys containing refractory metals, such as molybdenum, difficulties have been encountered in obtaining complete dissolution of the high melting point metal, such as molybdenum, in the base metal having a relatively much lower melting point, such as titanium base metal. Molybdenum is reported to have a melting point of 2617°C, as compared to a melting point of 1660°C for titanium. As a result of this incomplete dissolution, molybdenum particles, which have a specific gravity of 10,2, as compared to 4,5 for titanium, segregate and drop, in unmelted form, to the bottom of the molten titanium pool, and form inclusions in the ingot produced. These molybdenum inclusions carry over through any remelts, so that the final alloy produced is nonhomogeneous.

Complete dissolution or distribution of molybdenum, tantalum, niobium, tungsten, or other high melting point alloy component is desired, since a single undissolved, sizable inclusion of the refractory metal in the alloy ingot produced makes the alloy unfit for its intended use. Any such inclusions in a finished article subject to mechanical stress, as for example a turbine blade, jet engine, or other structural component, may, as a result of its stress raising character, cause the part to crack or rupture catastrophically.

Matters are further complicated where it is desired to produce homogeneous titanium base alloys containing substantial quantities of molybdenum, for example, greater than 45% molybdenum. High molybdenum inclusions in such alloys pose even greater problems to the homogeneity of the alloy and any subsequent remelts. Thus, it would be desirable to produce a high molybdenum-containing titanium alloy where the higher melting molybdenum is in solid solution with the titanium, thereby forming a lower melting homogeneous eutectic alloy which can be readily dissolved in any subsequent alloying to form a final titanium base alloy.

Various methods have been practiced to produce homogeneous titanium base alloys containing small amounts of molybdenum. **US-A 2,588,007** (Jaffee) discloses sintered titanium-molybdenum binary alloys containing less than 7,5% molybdenum, the balance being titanium. **US-A 2,938,789** (Jaffee) discloses that tita-

nium-molybdenum binary alloys containing between greater than 30% molybdenum and less than 40% molybdenum, the balance being titanium, are well known, but suggests that such binary alloys containing more than 45% molybdenum are unworkable and of little value commercially. Both above documents suggest the use of ternary additions to the titanium-molybdenum alloy to improve the properties of the final alloys. **US-A 3,269,825** (Vordahl) discloses vacuum, consumable electrode, arc melted homogeneous titanium base alloys containing between about 6% to 15% molybdenum with substantially complete dissolution of the molybdenum in the base alloy, thereby avoiding formation of molybdenum inclusions. However, mentioned document also uses ternary additions to attain such results in the final alloy. **US-A 3,552,947** (Peterson et al.) discloses vacuum, consumable electrode, arc melted titanium base alloys containing about 11,5% molybdenum having a homogeneous microstructure, but this method uses a low density, porous, sintered molybdenum agglomerates as the refractory alloying component to avoid segregation and ternary additions. **US-A 3,645,727** (Finlay et al.) discloses a ternary titanium base alloy from master alloys containing high amounts of molybdenum, such as 30% to 75% molybdenum, in which the master alloy is a lower melting alloy than molybdenum alone through ternary additions which aids in its later dissolution in titanium. **US-A 4,634,478** (Shimogori et al.) discloses a vacuum arc melted and annealed titanium base alloy containing 0,2 to 3,0% molybdenum, the balance being substantially titanium. **US-A 5,316,723** (Perfect) discloses a thermite titanium base master alloy containing substantial amounts of molybdenum, such as 55% to 75% molybdenum, and which also contains ternary additions to aid in its later dissolution in titanium.

Prior attempts to incorporate molybdenum in large quantities in alloys, particularly master alloys, where the base metal has a substantially lower melting point, such as titanium, have been generally unsuccessful in achieving alloy homogeneity. Typically, the homogeneity of the alloy is dictated by the alloying process used, and an acceptable process has not heretofore been designed to form substantially homogeneous titanium base master alloys containing large quantities of molybdenum. In addition the art has been guided away from producing titanium base alloys containing substantial amounts of molybdenum, since the dissolution problems encountered in the art are compounded with use of greater amounts of the refractory metal, and the alloy produced is also generally difficult to work even at elevated temperatures and difficult to produce in wrought condition for subsequent fabrication. What is needed is a method of producing a titanium base binary master alloy with relatively high amounts of refractory metals, such as molybdenum, tantalum, niobium, tungsten, with a substantially homogeneous microstructure.

It is an **object of the present invention** to provide a method of producing alloy compositions containing

lower melting metals having substantial quantities of refractory metals homogeneously incorporated therein. This is achieved according to claim 1.

With the invention a method is provided of obtaining substantially complete dissolution and/or distribution of refractory metals, such as molybdenum, tantalum, niobium, tungsten, in a relatively lower melting point base alloy, such as titanium base alloy.

A method is provided of producing titanium base binary master alloy compositions containing substantial quantities of refractory molybdenum or tantalum, in which the resultant alloy is homogeneous and, thus, available for subsequent alloying into an acceptable final titanium base alloy (claims 11 to 14).

Percentage given in the claims refer to weight percentage.

There are shown in the drawings certain exemplary embodiments of the invention as presently preferred.

FIGURE 1 is a scanning electron micrograph (SEM) of a cross-section of an ingot of a titanium-molybdenum binary master alloy produced in accordance with the method of the present invention, and exhibiting substantially no "free" molybdenum in its microstructure.

FIGURE 1a is an enlarged representation of Figure 1 as raster scanned print out.

FIGURE 2 is an energy dispersive x-ray spectrograph (EDS) of the titanium-molybdenum binary master alloy of FIGURE 1, showing a plot of intensity I versus energy E of x-rays given off by the master alloy bombarded by the electron beam of the SEM.

The examples of present invention are directed to a method of producing homogeneous alloy compositions, and the alloys produced thereby, which comprise lower melting base alloys containing substantial quantities of refractory metals uniformly and homogeneously distributed throughout the alloys. The present invention is not limited to a single, restricted class of alloys nor to any particular alloy composition.

The example of the method according to the invention is broadly useful in the production of nearly all alloys containing appreciable quantities of refractory metal, such as molybdenum, tantalum, niobium, tungsten, in a base metal having a melting point substantially lower than that of the refractory metal, such as titanium. It is especially useful in the production of titanium base alloys, in particular master alloys, containing high amounts of molybdenum, which for a variety of reasons are not commercially viable at this time.

However, exemplary of alloys produced from the practice of the method of the invention, the present invention provides homogeneous titanium base binary alloys containing substantial quantities of refractory molybdenum, preferably high molybdenum-containing

titanium base master alloys used for subsequent alloying with titanium and other metals to form a final titanium base alloy. In practicing the method of the invention, molybdenum, in powdered form, preferably, pure molybdenum metal powder, is intimately mixed in appropriate proportions with titanium, in powdered form, preferably pure titanium metal powder. The powder mixture is then pressed into a compact or briquette with application of pressures over about 7000 psi (490 kg/cm²) and preferably between about 15000 and 30000 psi (1055 kg/cm² to 2110 kg/cm²). Usually such compacts are formed in an isostatic press and within cylindrical rubber bags of approximately 12 inches (30,5 cm) in diameter and 32 inches (81 cm) in height.

The compacts are preferably formed in the shape of discs weighing between about 4,5 kg to 22,7 kg. The compacts are then stacked, one on top of the other, typically in a staggered overlapping array, in a furnace preferably having a controlled atmosphere, for example, a vacuum furnace with internal resistive heating elements or a vacuum induction furnace. For larger compacts, it is preferred to place spacers at intervals within the compact powdered charge before pressing in order to insure uniform compaction and produce more manageable alloy sizes. The spacers can be made from rubber. Furthermore, the spacers are constructed, typically with raised ridges on one side, so as to form grooves or scores in the compacts which facilitate subsequent breaking into pieces after alloying. The stacked compacts are alloyed by a "solid state fusion" reaction which occurs substantially in a solid state. It is believed that the compaction of the metal powders under pressure results in a high degree of intermingling of the grain boundary layers of the individual elements, somewhat akin to melting conditions, and thus when exposed to elevated temperatures, but below the individual element melting points, the compacted charge unexpectedly goes into solid solution and forms an alloy substantially free of inclusions of the refractory metal.

The stacked compacts are preferably placed in the furnace under vacuum or inert gas, such as argon. It is preferred that the furnace is heated to between about 250°C and 350°C, typically about 300°C, while under vacuum to drive off any retained moisture and gases and held at that temperature until the furnace vessel and compacts reach equilibrium. At such point argon or other inert gases can, if desired, be introduced into the furnace, preferably introduced to a pressure of between about 5 psi and 15 psi (0,35 kg/cm² to 1,05 kg/cm²). The temperature is then increased to between about 800°C and 1400°C, typically about 900°C for Mo/Ti, and held until equilibrium is reached within the compacts, actual time is dependent on size of load, during which time solid state alloying occurs. Of course, the alloying temperature and time will depend on the optimal solid state fusion temperature of the compact. No special pressure conditions are required for the alloying, which is usually carried out either in a vacuum or at about or slightly above atmospheric pressure.

Then, the fused compacts are allowed to cool to ambient temperature, preferably also under vacuum or inert gas, such as argon. Once cooled the fused compacts can be further processed, such as size reduced into broken pieces, typically by crushing, milling, grinding or otherwise comminuting, to form a powdered master alloy. The powdered master alloy can then be mixed with other alloying components, such as titanium, to form another charge and then subsequently alloyed to yield a final titanium base alloy.

In a preferred embodiment of the invention, the titanium-molybdenum binary master alloy produced comprises about 50% molybdenum, and the balance being titanium. In another embodiment, the titanium-molybdenum binary master alloy produced comprises between about 10% and 90% molybdenum, and the balance being titanium. In yet another embodiment, the titanium-molybdenum binary master alloy produced comprises between about 45 and 55% molybdenum, and the balance being titanium.

It is further preferred that the master alloy composition contain low gas impurities, that is, less than 0,5% oxygen, 0,2% nitrogen, and 0,1% hydrogen. Other impurities must be as low as possible and are directly dependent on raw material purity.

Unless otherwise specified, all percentages set forth herein refer to weight percent.

In accordance with practice of the process of this invention, the titanium-molybdenum master alloy produced thereby will be substantially homogeneous and molybdenum inclusions in the ingot will predominately not be present.

The invention will further be clarified by a consideration of the following non-limiting specific example, which is intended to be purely exemplary of the practice of invention used to produce titanium base binary master alloys containing high quantities of molybdenum.

EXAMPLE 1

A titanium base master alloy containing about 50% by weight molybdenum, the balance being titanium was prepared by the following process:

About 50 lbs. (22,75 kg) molybdenum powder was intimately mixed together with about 50 lbs. (22,75 kg) titanium powder for about 15 minutes to form a powdered charge. The powdered charge was then packed into a cylindrical rubber bag (9 in. dia. x 26 in. ht.; or 23 cm x 66 cm) with scored rubber spacers about every 20 lbs. (9 kg) apart and compacted at 25000 psi. (1760 kg/cm²) in an isostatic press to form 5 compacted discs weighing about 20 lbs. (9 kg) each disc. The compacted discs were then loaded in a vacuum furnace, stacked one on top of each other and were heated to about 950°C for about 47 hours and then allowed to cool to ambient temperature. After cooling, the fused, alloyed and stuck together Mo-Ti discs were separated and then each disc was crushed into smaller pieces in a crusher, a sample of which was submitted for analysis.

The compositional analysis is provided below.

(Table 1)

RAI Analysis SAMPLE NUMBER VIM2-300	
Element	Weight %
Mo	49,71
Ti	49,71
Al	0,014
C	0,24
Cr	0,005
H	0,003
Fe	0,185
Mg	0,002
N	0,009
O	0,166
S	0,003
Sn	0,002
W	0,0004

FIGURES 1, 1a and 2 represent the structural and compositional analysis of the master alloy produced in EXAMPLE 1. The represented master alloy being substantially homogenous.

EXAMPLE 2

Example 2 was a scaled up repeat of Example 1 using 250 lbs. (113,4 kg) of molybdenum powder and 250 lbs. (113,4 kg) of Titanium powder. The compositional analysis is provided below.

(Table 2)

RAI ANALYSIS VIM3-002	
Element	Weight %
Mo	50,08
Ti	49,19
Al	0,01
C	0,027
H	0,002
Fe	0,041
N	0,130
O	0,243
S	0,001
W	0,0003

(Table 3)

RAI ANALYSIS VIM2-304	
Element	Weight %
Ta	47,93
Ti	50,97
Al	0,331
C	0,063
H	0,1802
Fe	0,013
N	0,088
O	0,476
S	0,001
W	0,0003

EXAMPLE 3**Tantalum/Titanium**

A titanium based master alloy containing approximately 50% Ta and 50% Ti was prepared by the following process. About 5 pounds (2,27 kg) of Ta powder was intimately mixed with about 5 pounds (2,27 kg) of Ti powder for about 15 minutes to form a powdered charge. The powdered charge was then packed into a cylindrical rubber bag (23 x 66 cm) with scored rubber spacers about every 20 lbs. (9 kg) apart and compacted at 25000 psi. (1760 kg/cm²) in an isostatic press to form 5 compacted discs weighing about 20 lbs. (9 kg) each disc. The compacted discs were then loaded in a vacuum furnace, stacked one on top of each other and were heated to about 1400°C for several hours and then allowed to cool to ambient temperature. After cooling, the fused, alloyed and stuck together Ta-Ti discs were separated and then each disc was crushed into smaller pieces in a crusher, a sample of which was submitted for analysis. The compositional analysis is provided below.

The invention having been disclosed in connection with the foregoing variations and examples, additional variations will now be apparent to persons skilled in the art. The invention is not intended to be limited to the variations specifically mentioned.

Claims

1. **Method** for producing a substantially homogeneous titanium base master alloy containing substantial quantities of molybdenum, comprising the steps:

- (a) admixing powdered molybdenum with powdered titanium in appropriate proportions to produce a powdered charge;
- (b) pressing the powdered charge to the form of a briquette;
- (c) alloying in a solid state the briquette until substantially homogeneous to form a resultant titanium-molybdenum master alloy; and,
- (d) solidifying the resultant master alloy by cooling.

2. Method of Claim 1, further comprising the step of:

- (e) size reducing said resultant master alloy to powder form for further alloying with titanium.

3. Method of Claim 1 or 2, in which the alloying step (c) occurs in a furnace in an inert gas.

4. Method of one of the Claims 1 to 3, in which the alloying step (c) occurs in a vacuum.

5. Method of one of preceding Claims, in which the

alloying step (c) occurs at an elevated temperature but below the individual melting point of the metal powders, preferably between about 800°C and 1400°C, preferably about 1050°C.

sions.

- 5
6. Method of one of preceding Claims, in which the pressing step (b) includes isostatic pressing at pressures in excess of 7000 psi (above 490 kg/cm²).
10
7. Method of one of preceding Claims, in which the pressing step (b) forms briquettes in the form of cylindrical discs of from about 10 to 50 pounds of weight (4,5 kg to 22,7 kg).
15
8. Method of one of preceding Claims, in which the powdered alloying components of admixing step (a) comprise pure molybdenum and titanium metal powders.
20
9. Method of Claim 2, in which the size reducing step (e) includes size reducing by crushing, milling or grinding.
25
10. The method of Claim 2 or 9, which further comprises the steps of:
 - (f) admixing the powdered resultant master alloy with at least powdered titanium to form a powdered charge; and,
30
 - (g) alloying said powdered charge to form a final titanium base alloy containing molybdenum.
- 35
11. **Titanium base binary master alloy** produced according to the method of one of aforementioned claims, comprising about 45% to 55%, preferably about 50% molybdenum, and the balance substantially titanium.
40
12. Titanium base binary master alloy produced according to the method of Claim 1, comprising between about 10% and 90% molybdenum, and the balance substantially titanium.
45
13. Substantially homogeneous titanium base binary master alloy containing substantial quantities of molybdenum, which comprises:
 - from about 45% to 55% molybdenum, and the balance substantially titanium, said alloy being characterized by being substantially free of molybdenum inclusions.
50
- 55
14. Substantially homogeneous titanium base binary master alloy containing substantial quantities from about 40% to 60% of tantalum, and the balance substantially titanium, said alloy being characterized by being substantially free of tantalum inclu-

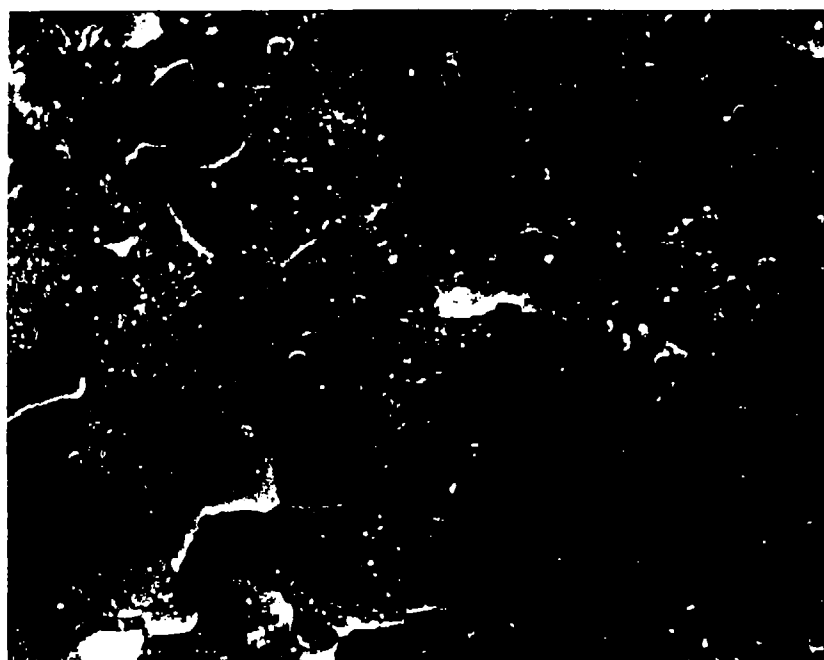


FIG. 1

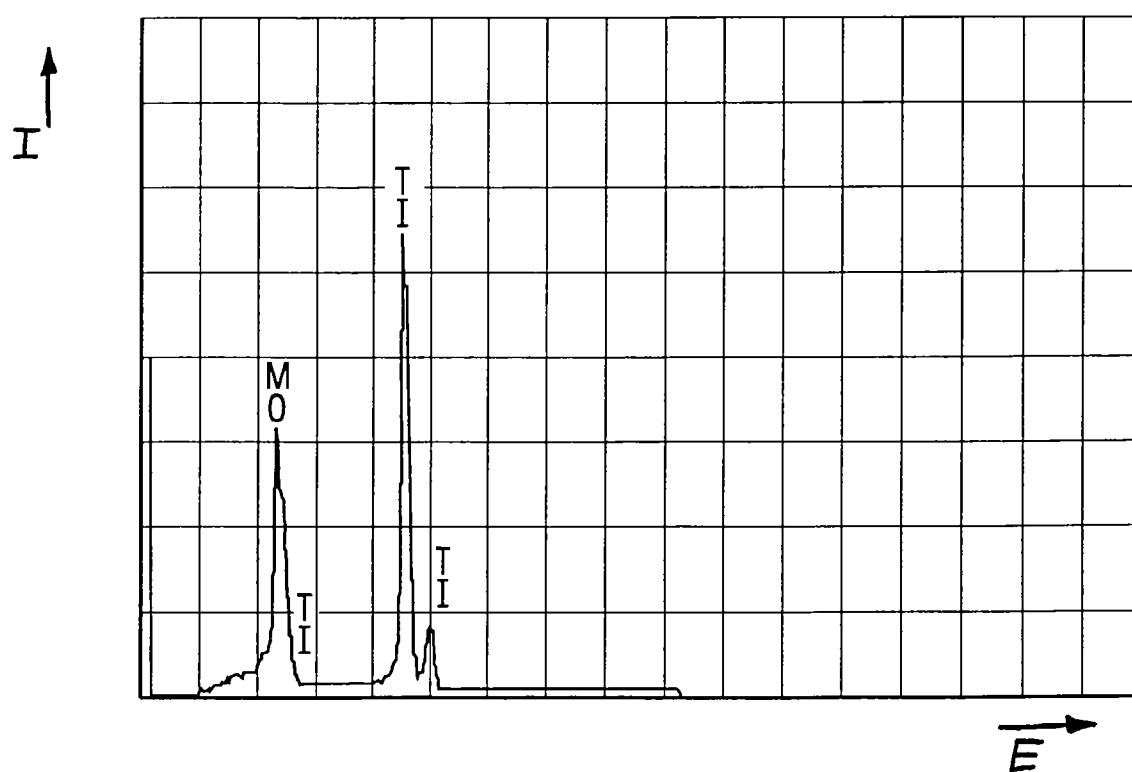


FIG. 2

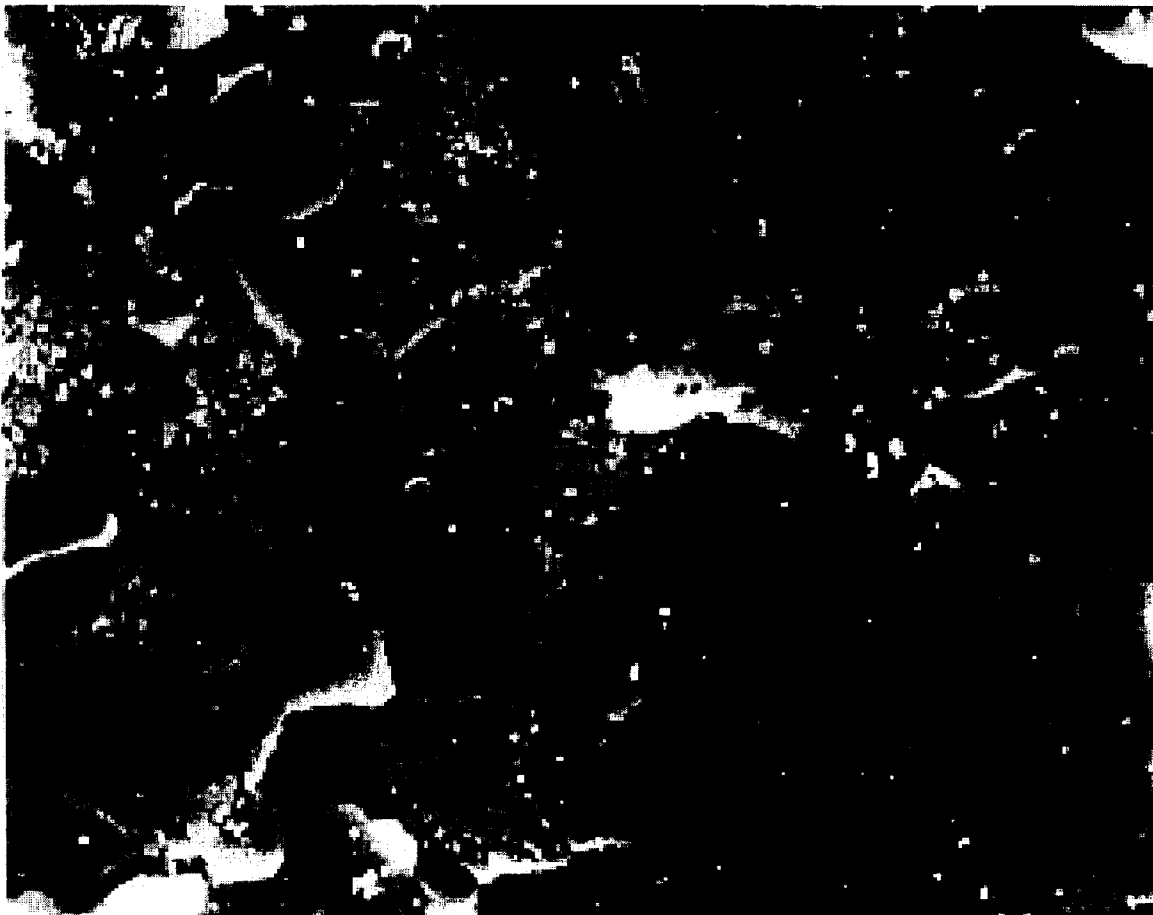


Fig. 1a