行政院國家科學委員會補助專題研究計畫 ☑ 成果報告
□期中進度報告

發展重力場分流薄層分離技術在拋光物質分離的應用

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中文摘要

分流薄層分離技術(SPLITT Fractionation)近年來已發展成為分析、純化分離之有用技術，SF可依分離樣品性質，選擇不同的分離場(driving forces)，如電場、重力場、磁場等，分流薄層分離技術除了分析(Analytical SF)之應用，亦可用於準備（純化分離，preparative SF）用，其中以重力場(gravitational SF)最為簡單、最方便。重力場分流薄層分離技術最佳應用之一，即是高密度(density > 1.5 g/ml)微粒物質之分離，如 latex beads。本計畫利用重力場分流薄層分離技術發展簡單、快速、準確之拋光劑顆粒分離(narrowing size distribution)，尤其是小於 5 μm 微粒物質，如金剛石系(diamond abrasives)、氧化鈰系(cerium oxide abrasives)、氧化鋁系(alumina oxide abrasive)。實驗結果無論從顯微鏡攝影所觀察之顆粒大小、或軟體計算顆粒分佈均顯示簡單的重力場分流薄層分離技術(gravitational SF)可成功地應用於移除過大之拋光物質顆粒，適當地增加薄層之長度與寬度可增加分離的量(scaling up)，於拋光物質工業之品管上具有頗大的應用潛力。

關鍵字：分流薄層分離技術、顆粒分離技術、拋光物質

Abstract

Split-flow Thin (SPLITT) fractionation is a new family of separation techniques for macromolecules, colloids, and particles. Gravitational SPLITT fractionation is the choice for separation of dense and micron sized particles due to its simple and easy instrumentation. One of the important applications from gravitational SPLITT fractionation is on abrasive materials because the size distribution of abrasive materials is crucial to their performance and applications. Gravitational SPLITT fractionation was used for removing the oversized particles and narrowing the size distribution of abrasive materials using diamond, cerium oxide and aluminum oxide as examples. The cut-off sizes on these abrasive materials were tested with a throughput about 3.0 g/hr for removing the oversized particles. The size distributions of fractionated sample and photomicrographs show successful applications in removing the oversized particles. Scaling up the throughput of SPLITT fractionation is feasible by increasing the channel length and channel breadth. Gravitational SPLITT fractionation is very promising for applications of abrasive material industry in removing oversized particles and narrowing their size distributions.

Keywords：Split-flow Thin (SPLITT) fractionation、particle separation、 abrasive particles

一、緣由與目的

研磨拋光劑主要功能用於金屬表面亮度、輕微刮傷處理，藉由研磨粒子拋除製程所留下之微缺陷或傷痕；表面拋光劑亦可在金屬表面形成一層保護層，防止油漆氧化和受損。 精密拋光劑主要應用於半導體、電子、光學玻璃及精密金屬研磨工業。高品質的精密研磨粉，所有產品均需經過嚴緊的粒度篩選及品管控制，研磨拋光劑顆粒大小與拋光結果有密切關聯，如顆粒大小在 90~30 μ 作為粗仕研削用， 在 15~9 μ 作為一般亮度用，6~3 μ 作為精密亮度用，1~0.25 μ 則作為超鏡面拋亮 。進年來半導體製造技術的更新快速，五年來已由 0.6 微米至現今的 0.175 微米，下一步更將向 0.13 微米邁進。製程技術快速演進的關鍵在於研磨液，拋光是晶圓表面加工的最後一道步驟，移除量約 10-20μ，其目的在改善前製程所留下之微缺陷，並獲得一平坦度極佳的晶圓以滿足 IC 製程的需求，拋光時要依需求選擇正確的拋光布搭配適當的拋光劑，才可得到最佳的拋光效果。

金剛石系列採用最高品質的單晶體金剛石，適合作藍寶石、陶瓷、鋼及超硬金屬等拋光；氧化鈰系列適合作光學鏡頭，LCD，石英及光學玻璃等拋光；氧化鋁系列傳統磨料研磨產品，現已廣泛被使用於金屬、塑膠、模具、電子、電腦、精密零件及超硬材料等行業；碳化矽系列適合作石英切割，金屬研磨及精密噴砂等作業。由此可見拋光劑的開發在精密電子、光電產業之重要性，而嚴緊的粒度篩選，緊密的分佈及形狀控制則是品質的保證。

分流薄層分離技術(SPLITT Fractionation)近年來已發展成為分析、純化分離之有用技術[1~7]，SF 可依分離樣品性質，選擇不同的分離場(driving forces)，如電場、重力場、磁場等，分流薄層分離技術除了分析(Analytical SF)之應用，亦可用於準備（純化分離，preparative SF）用 [7~8]，其中以重力場(gravitational SF)最為簡單、最方便。重力場分流薄層分離技術最佳應用之一，即是高密度(density > 1.5 g/ml)微粒物質之分離，如 latex beads [7,9]。常用之顆粒(particle)分離技術，如篩濾(sieving)方法，在 5 μ 以下之顆粒分離其準確度只有±10%，因此本計畫的目的在利用重力場分流薄層分離技術發展簡單、快速、準確之拋光劑顆粒分離(narrowing size distribution)，尤其是小於 5 μ 微粒物質。

二、文獻探討

The theory on SF operation and cutoff diameter (d_c) has been previously shown in literature[1,4,5,8]. Here we only summarize the required results as a background for calculation used in this study. The volumetric flowrate of filament traversed by the particles is given by

$$\Delta \dot{V} = bLU \qquad (1)$$

where b is the channel breadth, U is the field induced velocity on sample, and L is the channel length measured between the inlet and outlet splitting edges. When transport is driven by gravity as in this study, U is given by

$$U = G\frac{(\rho_p - \rho)d^2}{18\eta} \qquad (2)$$

Where G is gravitational acceleration, ρ_p is the particle density, ρ is the carrier density, η is the carrier viscosity, and d is the diameter of spherical (or equivalent) particle. The substitution of equation 2 into equation 1, we get

$$\Delta \dot{V} = bLG\frac{(\rho_P - \rho)d^2}{18\eta} \quad (3)$$

The important thing is the relative magnitude of $\Delta \dot{V}$ and $\dot{V}(t)$, the latter being the volumetric flowrate of the transport lamina. It can be expressed as

$$\dot{V}(t) = \dot{V}(a) - \dot{V}(a') = \dot{V}(b') - \dot{V}(b) \quad (4)$$

where $\dot{V}(a)$ and $\dot{V}(b)$ are volumetric flowrates of outlet a and b, and $\dot{V}(a')$ and $\dot{V}(b')$ are the volumetric flowrates of inlet a′ and b′, respectively. For present purposes, we assume that all particles for which $\Delta \dot{V} > \dot{V}(t)$ will emerge from outlet b. Particles of less or equal to $\Delta \dot{V}$, such that $\Delta \dot{V} \le \dot{V}(t)$, will emerge from outlet a. Therefore the cutoff value of $\Delta \dot{V}$ is given by

$$\Delta \dot{V}_c = \dot{V}(t) \quad (5)$$

The cutoff value $\Delta \dot{V}_c$ specifies the cutoff diameter d_c. Thus from equations 3 and 5, we get

$$\dot{V}(t) = \Delta \dot{V}_C = bLG\frac{(\rho_P - \rho)d_c^{\,2}}{18\eta} \quad (6)$$

and d_c is therefore expressed by

$$d_c = \left\{\frac{18\eta \dot{V}(t)}{bLG(\rho_P - \rho)}\right\}^{1/2} \quad (7)$$

In principle, all particles smaller than or equal to d_c exit at outlet a while particle larger than d_c exit at outlet b. The cutoff diameter d_c can be adjusted by tuning the flowrates of inlet and outlet substreams according to equations 4 and 7.

三、研究方法

The channel length and breadth of the channel used in this study were 20 cm and 4 cm, respectively. For removing the oversized particles, the channel thickness consisted of top spacer (0.0127 cm), splitter (0.0127 cm), and bottom spacer (0.0127 cm) with a total thickness of 0.0381 cm. The calculated void volume of this channel was 3.05mL. Operation was carried out at the ambient laboratory temperature of 23 ± 0.3°C. The carrier solutions used for CSF experiment were 0.1% sodium hexametaphosphate (Aldrich, Milwaukee, WI, USA) in the deionized water with a density of 0.998 g/mL. The diamond abrasive with density of 3.51 g/mL was obtained from Struers (Westlake, OH, USA). The aluminum oxide abrasive with density of 3.99 g/mL and the cerium oxide abrasive with density of 7.13 g/mL were obtained from Aldrich (Milwaukee, WI, USA). A Teflon rotary valve 5025 with loop volume of 3.5 mL from Rheodyne (Cotati, CA, USA) was used for sample injection in optimization experiment. A LC pump (SSI series II, State College, PA, USA) and a QD-0 pump (FMI, Oyster, NY, USA) were used for most of the experiments. A micro-tubing pump (Eyela, MP-3, Rikakikai, Tokyo, Japan) was used for the continuous sample introduction of abrasive particles in the CSF experiment. Mylar strips were placed symmetrically on the splitter in all of this study.

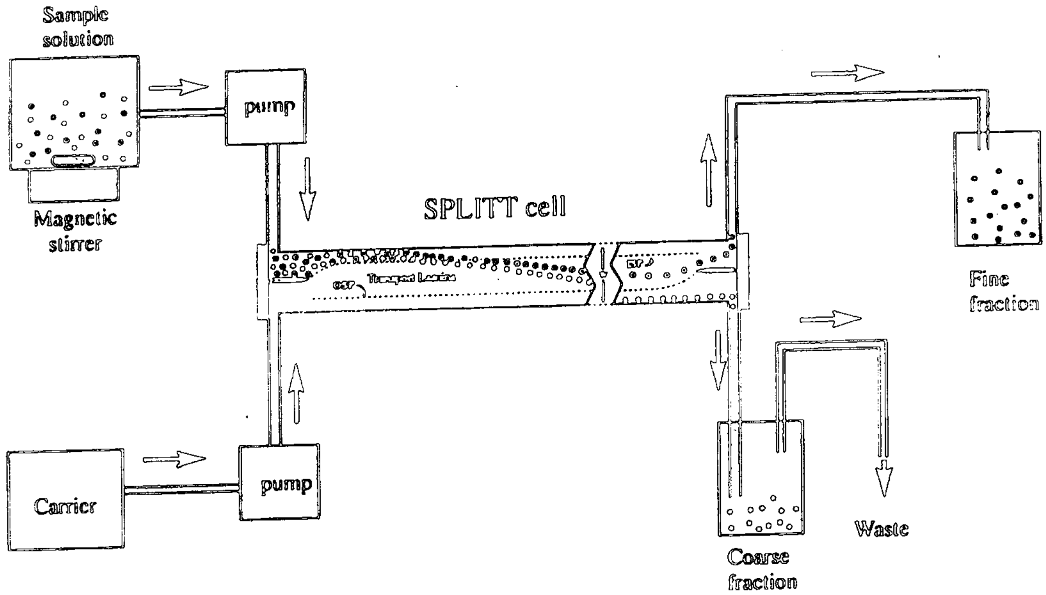

Figure 1 Schematic diagram of gravitational SPLITT fractionation

The fractional retrieval of sample emerging from outlet b, Fb, (and thus the fraction with diameter $d > d_c$) was calculated from the following equation

$$Fb = \frac{N_b}{N_a + N_b} \tag{8}$$

where N_a and N_b are the number of particles exiting at outlets a and b respectively. It is clear mathematically that the sum of Fa and Fb is equal to 1.

Image-Pro Plus software (Silver Spring, MD, USA) was used to evaluate the size distribution of abrasive particles before and after SF operation. The particle images are taken from different portions of slides, a minimal number of 400 particles were counted in each fraction. Size selectivity (Sd) was defined as quantity of size d entering the coarse fraction divided by particle of size d in feed [14].

四、結果與討論

The applicability of SF on abrasive materials was illustrated with diamond, cerium oxide, and alumina oxide abrasives. The particle size distributions of original and fractionated abrasives were analyzed using Image-Pro Plus software as described in the experimental section.

Diamond abrasives

The SF of diamond was used to narrow its size distribution for better product performance.

The purpose was to remove the oversized particles with diameters greater than 3.8 μm. The appropriate flow conditions calculated from equation 7 with $\Delta\rho = 2.53$ g/mL are $\dot{V}(a')$=5.0 mL/min., $\dot{V}(b')$=20.0 mL/min., $\dot{V}(a)$=15.0 mL/min., $\dot{V}(b)$=10.0 mL/min. These flow rate conditions were used in removing oversized diamond abrasives in SF. The photomicrographs and particle size distributions of diamond abrasives before and after SF are shown in Figure 2. It is clear that the oversized particles are removed efficiently even with small leakage from small particles. The size distributions of original mixture and the collected fractions of diamond shown in Figure 2, indicate good fractionation.

<u>Cerium oxide abrasives</u>

Figure 3 shows photomicrographs and particle size distributions of cerium oxide abrasives before and after gravitational SF with cutoff size (dc) of 3.4μm. The flow rate conditions used were $\dot{V}(a')$=5.0 ml/min $\dot{V}(b')$=20.0 ml/min $\dot{V}(a)$=20.0 ml/min, and $\dot{V}(b')$=5.0 ml/min. The flow rate conditions and $\Delta\rho$(6.15ml/min) of cerium oxide abrasives were consistent with equation 7. The oversized particles were also removed effectively, as show in Figure 3.

<u>Alumina Oxide abrasives</u>

Figure 4 shows photomicrographs and particle size distributions of alumina oxide abrasive before and after gravitational SF with cutoff size (dc) of 4.4 μm. The flow rate conditions used were $\dot{V}(a')$=5.0 ml/min $\dot{V}(b')$=20.0 ml/min $\dot{V}(a)$=20.0 ml/min, and $\dot{V}(b)$=5.0 ml/min. These flow rate conditions were also consistent with theory as in equation 7.

Figure 5 shows the fractional retrieval of sample emerging from outlet b, Fb. It is clear demonstrated the cutoff size *(dc)* is 3.8 μm for diamond abrasives, 3.4 μm for cerium oxide abrasives, and 4.4 μm for alumina oxide abrasives.

The results confirmed that Gravitational SPLITT fractionation is useful for removing the oversized particles and narrowing the size distribution of abrasive materials using diamond, cerium oxide and aluminum oxide. The size distributions of fractionated sample and photomicrographs show very successful applications in removing the oversized particles. Scaling up the throughput of SPLITT fractionation is feasible by increasing the channel length and channel breadth. Gravitational SPLITT fractionation is very promising for applications of abrasive material industry in removing oversized particles and narrowing their size distributions.

五、計畫成果自評

本計畫研究成果內容與原計畫目標相符，由於計畫主持人所屬單位為新成立單位，雖然實驗室建製工程延誤，但在計畫延期的期限內仍達成原計畫設定的預期目標（如下所示）：

1. 預期完成之工作項目：

   完成自製分流薄層分離槽及組裝，並應用於拋光物質(abrasive material)顆粒大小之分離(narrowing size distribution)。

2. 對於學術研究、國家發展及其他應用方面預期之貢獻：

   發展自製分流薄層分離槽並以簡單的材料完成 ，可節省外購的經費，提供顆粒物質分離另一可行之技術及其他應用之參考。

3. 對於參與之工作人員，預期可獲之訓練：

   參與之工作人員從自行裝配分離槽的過程中，學得薄層分離槽的製造技巧，由實驗操作瞭解重力場應用於分離技術之原理及分析方法確效(Analytical Method Validation)之作法，並由實驗結果之處理學習統計分析。

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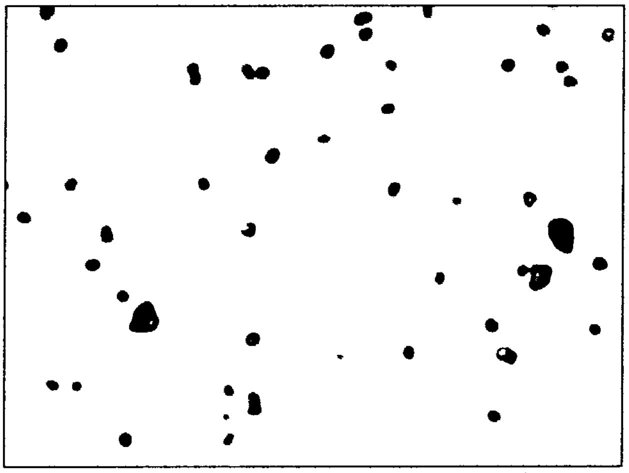
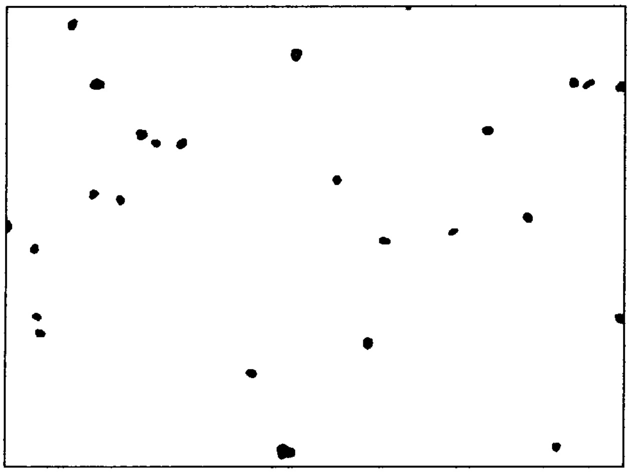
Figure 2 Photomicrographs of diamond abrasive before and after gravitational SPLITT fractionation

Diamond：Original



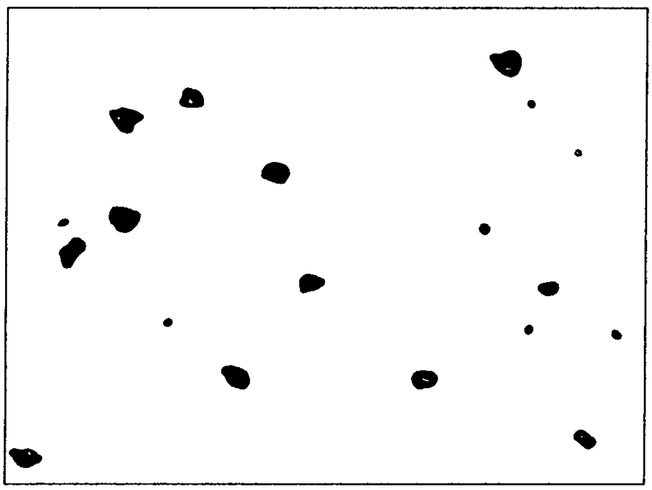
400x 10 μm

Diamond：Upstream fraction



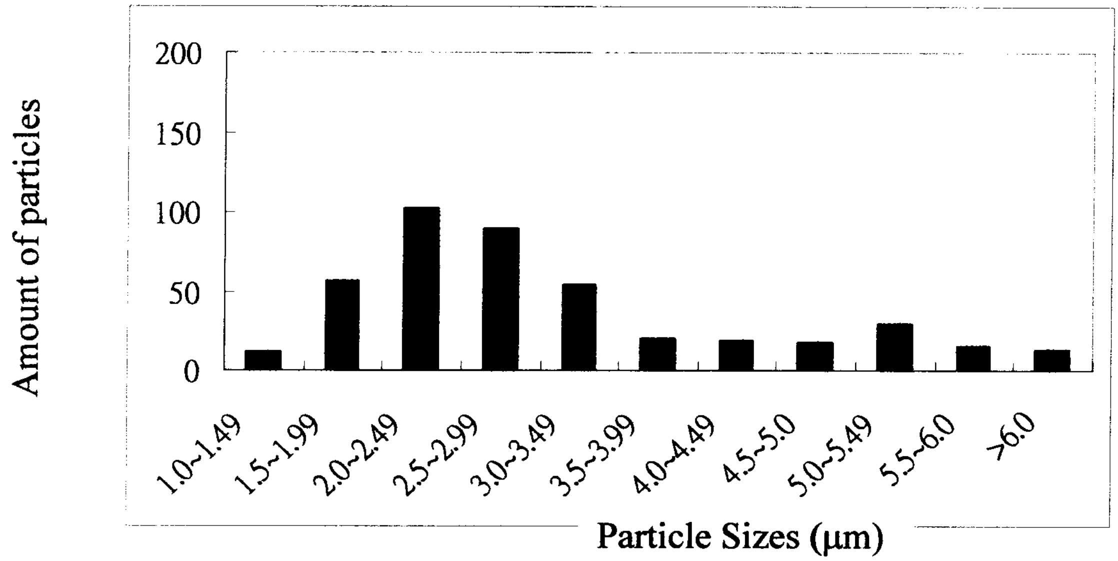
400x 10 μm

Diamond：Downstream fraction

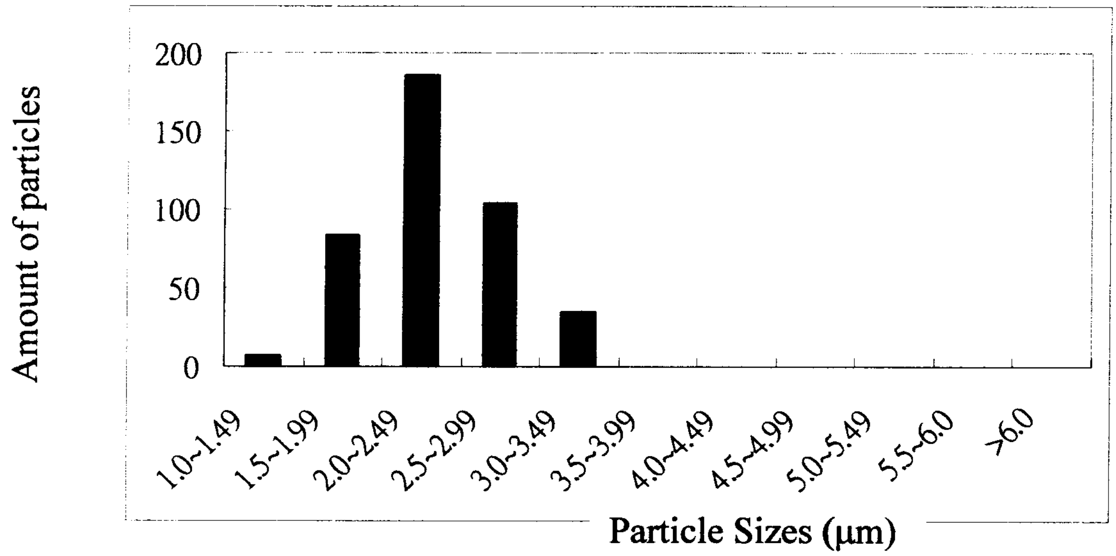


400x 10 μm

Diamond : Original



Diamond : Upstream fraction



Diamond : Downstream fraction

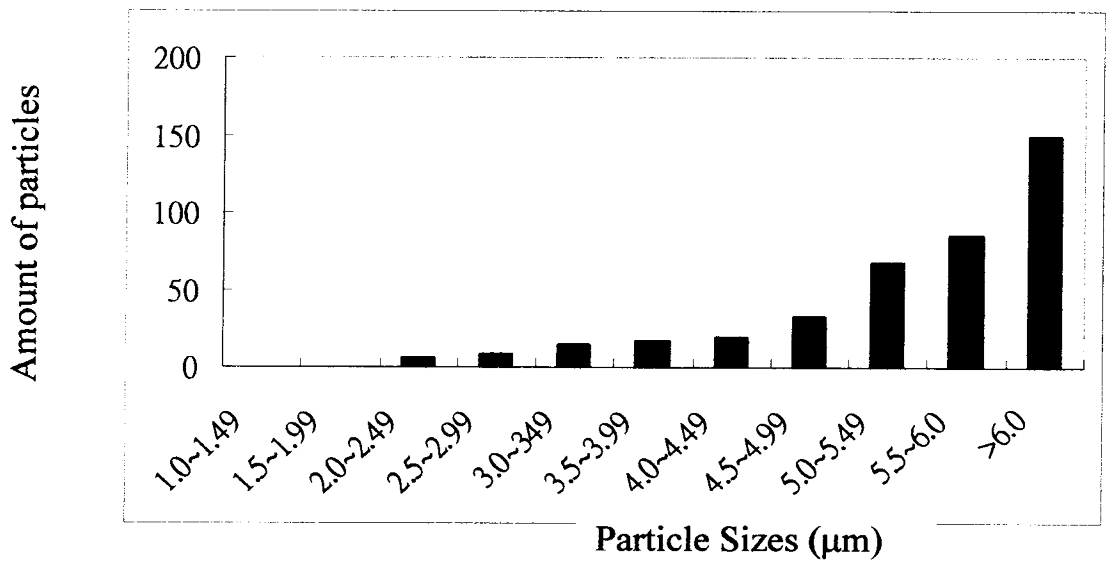
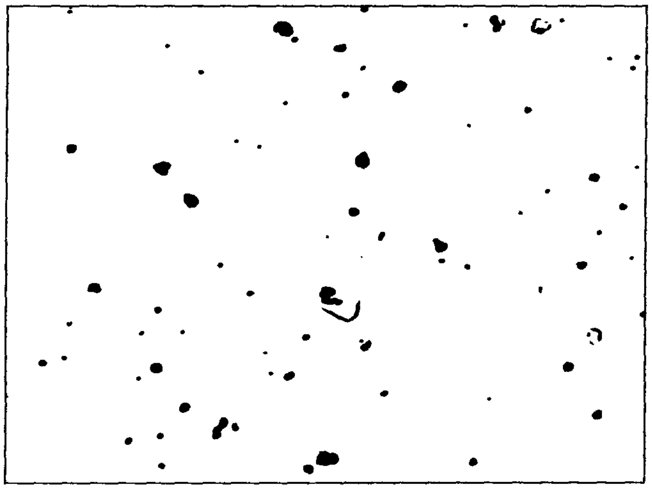


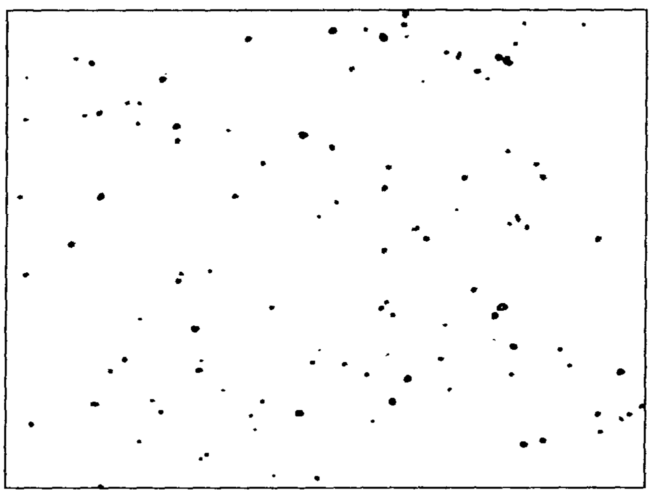
Figure 3 Photomicrographs of cerium oxide abrasive before and after gravitational SPLITT fractionation

Cerium(IV) oxide：Original



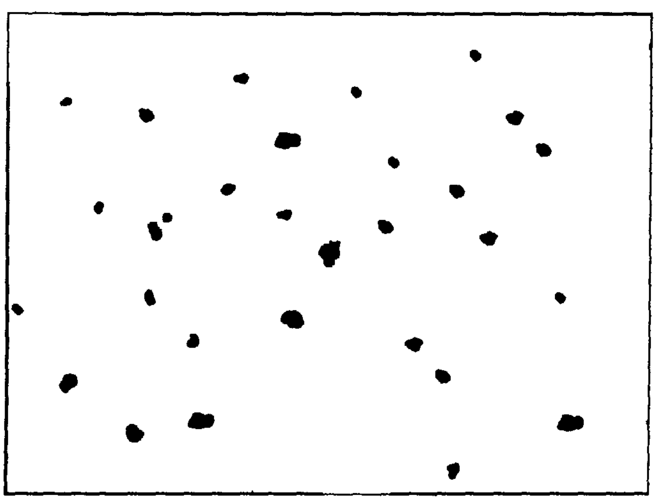
400x　　10 μm

Cerium(IV) oxide：Upstream fraction



400x　　10 μm

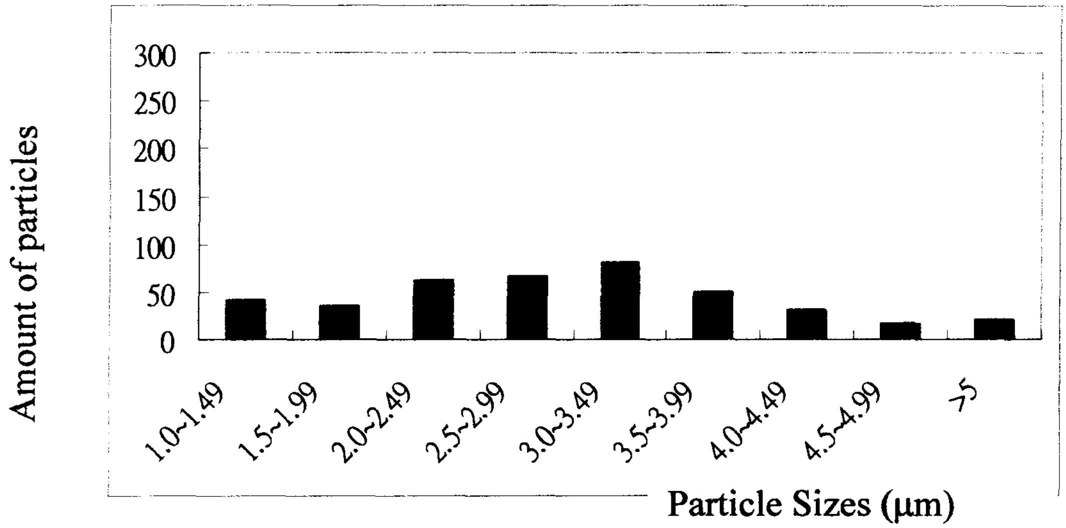
Cerium(IV) oxide：Downstream fraction



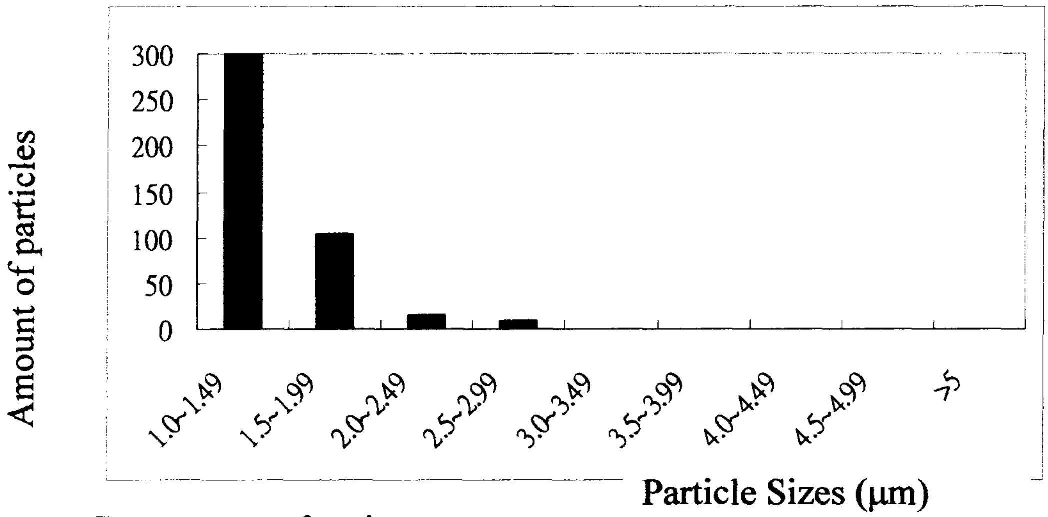
400x　　10 μm

Cerium(IV) oxide

Original



Upstream fraction



Downstream fraction

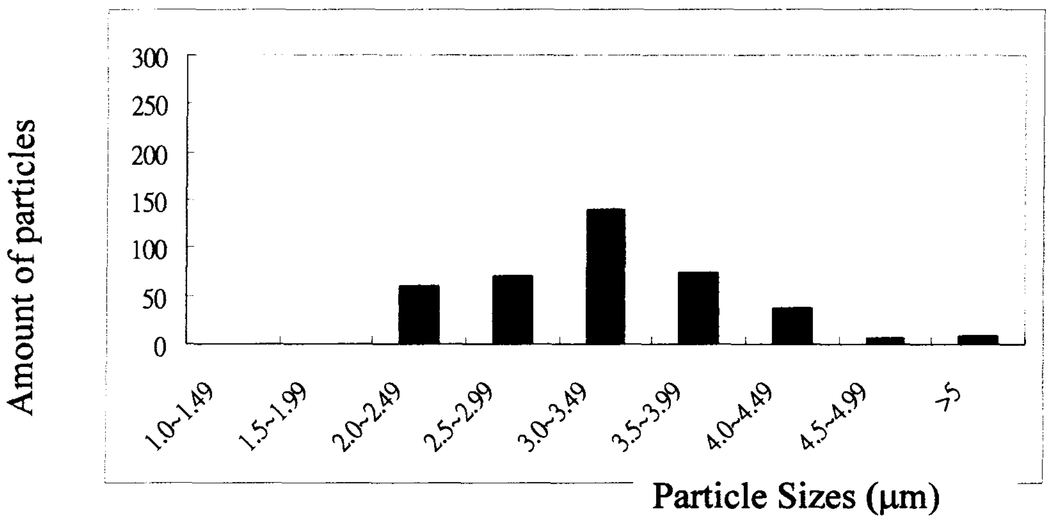


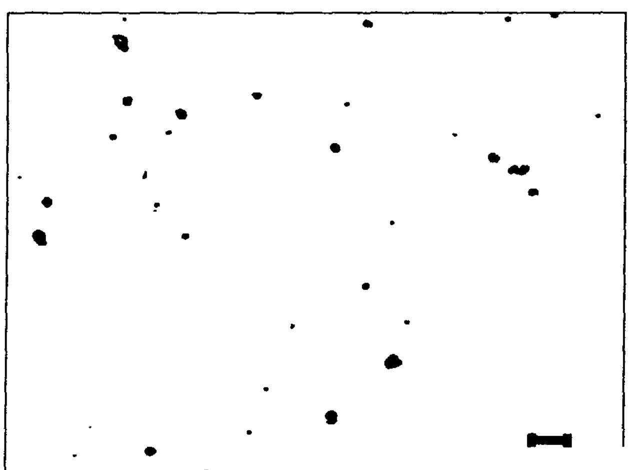
Figure 4 Photomicrographs of alumina oxide abrasive before and after gravitational SPLITT fractionation

Alpha Alumina : Original

400x

10μm

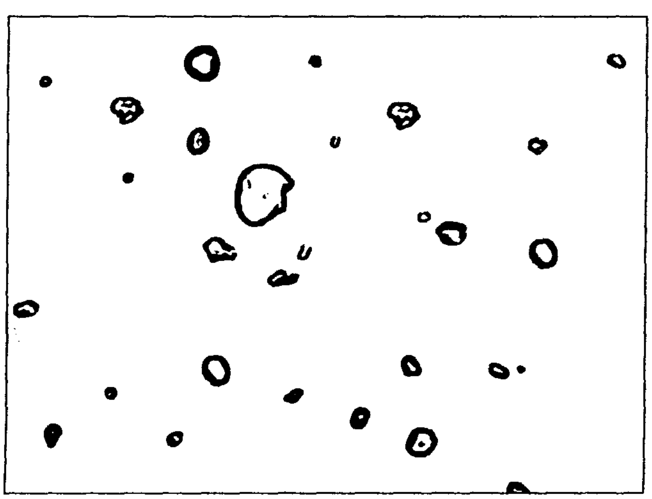
Alpha Alumina : Upstream fraction



10μm

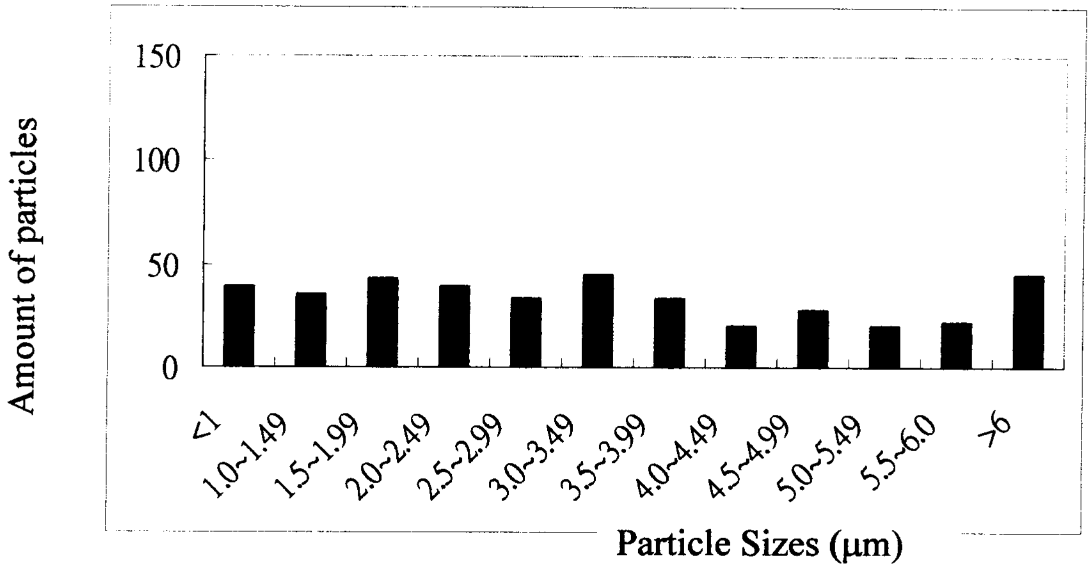
400x

Alpha Alumina : Downstream fraction

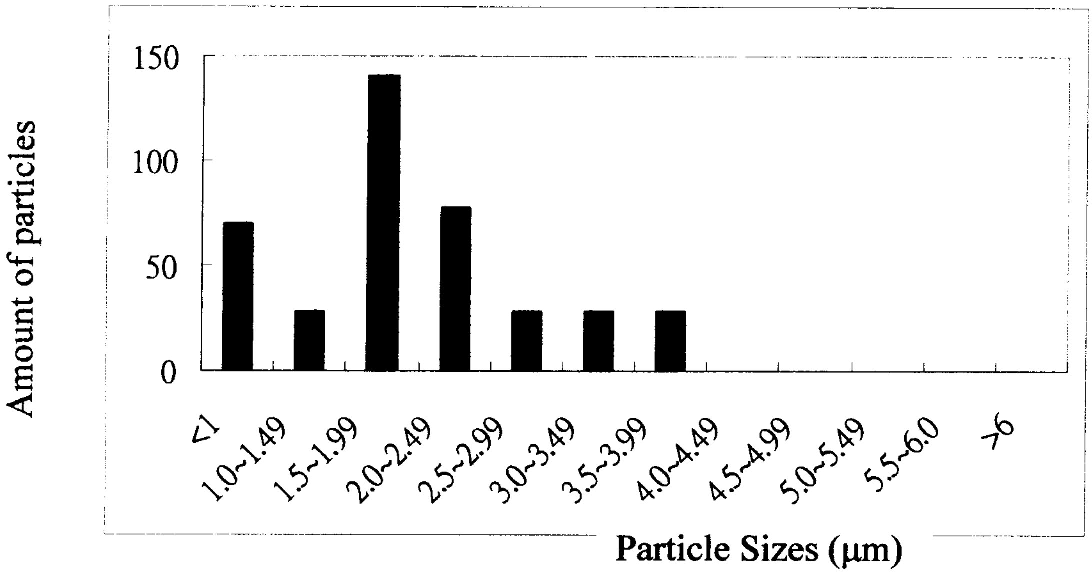


Alpha alumina-figure 4

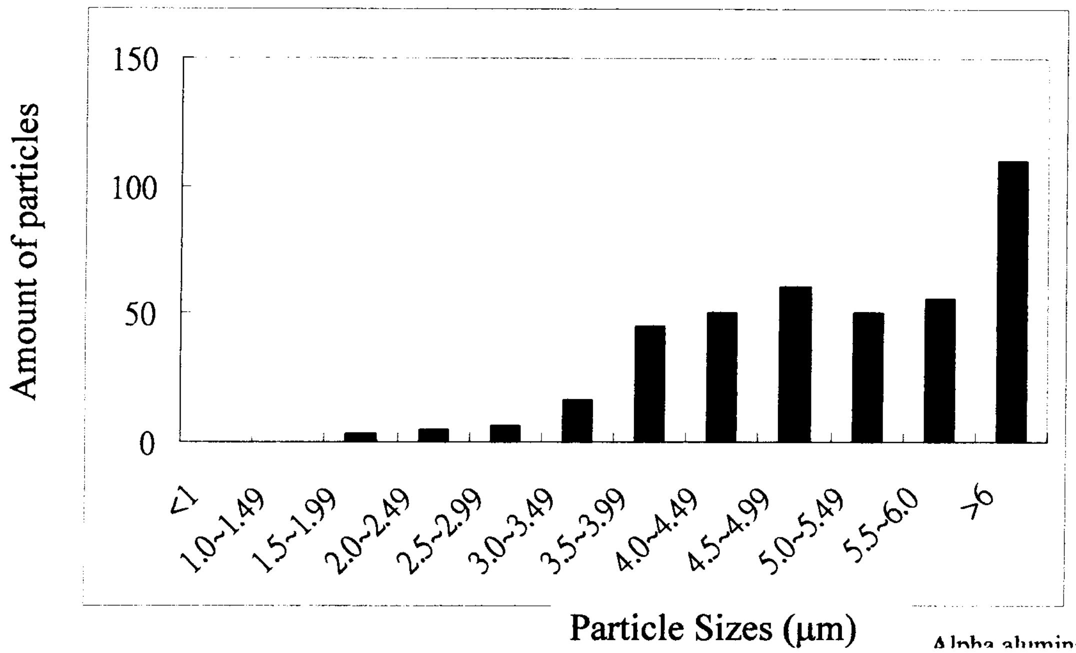
Alpha alumina： Original



Alpha alumina：Upstream fraction



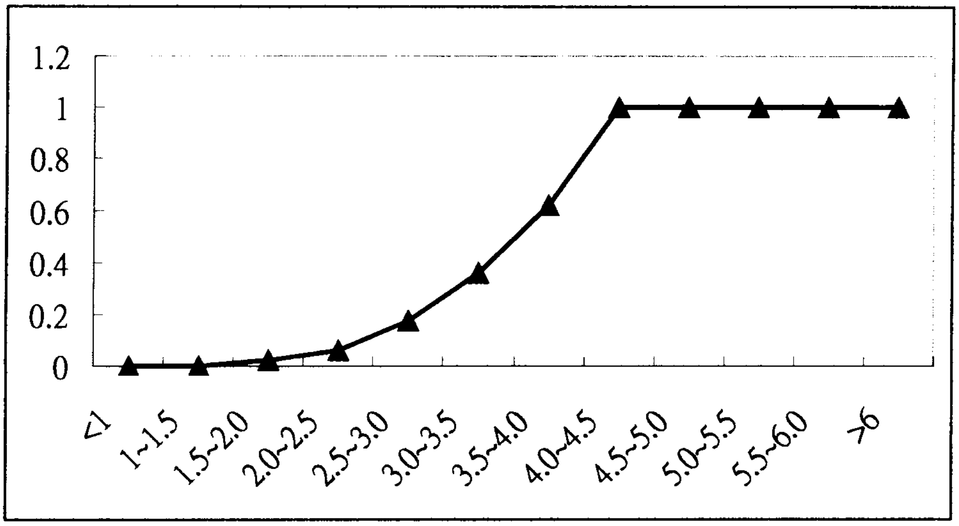
Alpha alumina：Downstream fraction



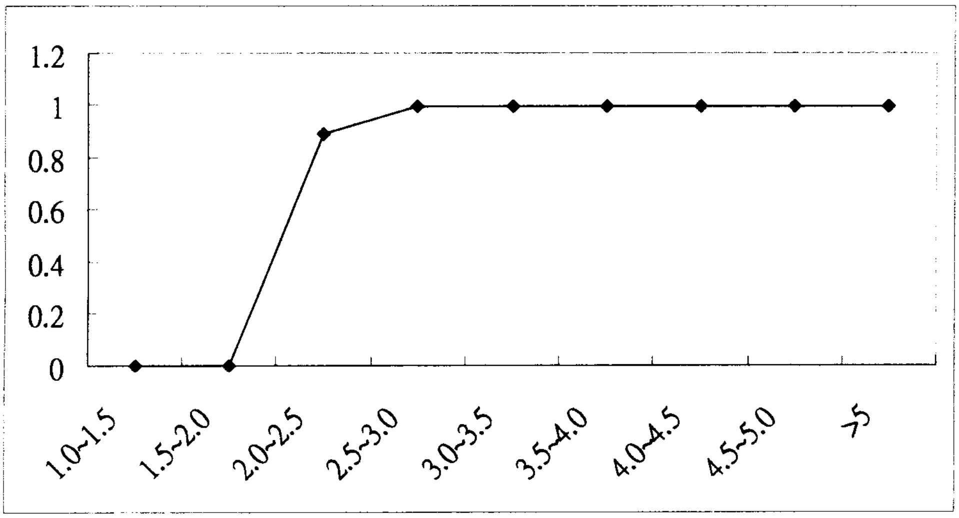
Alpha alumina-figure 4

Figure 5 The fractional retrieval of sample emerging from outlet b, (Fb)

Alumina oxide



Cerium oxide



Diamond