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高功率密度激光电离飞行时间质谱仪用于固体样品
一维、二维和三维元素分布的研究

The Study of One-dimensional, Two-dimensional and
Three-dimensional Elemental Distribution in Solids Using High
Irradiance Laser Ionization Time-of-Flight Mass Spectrometry

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摘 要

随着材料科学的快速发展,传统的基于溶液的分析方法因为其繁琐的样品前处理、易引入污染以及只能提供样品整体的组成信息等不足已经远远满足不了现代科学的需求,因此发展固体直接分析法一直备受关注。

本课题组自行研制的低压氦气辅助高功率密度激光电离飞行时间质谱(LI-TOFMS)被证实是一项非常优越的固体直接分析技术,应用范围涵盖了导体,半导体和非导体领域,可以同时进行包括非金属元素在内的多元素快速分析;此外,该项技术还可以实现无标准样品校准的半定量分析,这在固体直接分析中是非常关键的,因为基质匹配的固体标准样品一般难以获得。本论文主要是基于该项技术发展其对实际固体样品组成的空间分布分析方法,其中包括有一维元素分布分析、二维元素分布分析和三维元素分布分析,这三部分研究内容简要介绍如下:

1、一维元素分布分析

该项研究利用扩束镜和光阑来提取能量相对均一的脉冲激光中心光斑,并将其应用于薄层深度分析的均一溅射取样。首先利用纳秒激光电离飞行时间质谱(ns-LI-TOFMS)对单镀层和多镀层的薄层样品进行深度分析,并获得的激光平均溅射速率($AAR(Zn) = 1.3 \mu m/pulse$)和深度分辨率($\Delta Z(Zn) = 2.4 \mu m$)均为微米水平。为了进一步优化该项技术的深度分辨率,我们引入飞秒激光,并对比了两种激光模式(纳秒和飞秒激光)下的深度分析能力,结果表明飞秒激光电离飞行时间质谱获得的溅射速率($AAR(Pd) = 55 nm/pulse$)和深度分辨率($\Delta Z(Pd) = 310 nm$)均比纳秒激光优越了一个数量级;此外该项技术不仅可以应用于导体薄层样品的深度分析,还可实现对非导体薄层的深度分析。

2、二维元素分布分析

该部分内容是基于低压氦气辅助高功率飞秒激光电离飞行时间质谱(fs-LI-TOFMS)建立二维成像系统,首先对古代青瓷剖面进行2D元素成像,由青瓷剖面的瓷釉—过渡层—瓷胎三层结构的二维元素分布,据此探索了瓷胎和瓷釉之间的反应层的形成机理。其次,对唐代、五代、北宋和现代这几个不同文化时期的越窑青瓷的瓷釉和瓷胎进行了元素特征研究,瓷胎中被同时检测到的元素高达

29 个，瓷釉多达 25 个。其中瓷胎中的 Fe 和 Ti 以及瓷釉中的 Ca、P、Mn 和 Mg 可以作为区分不同朝代陶瓷的特征元素，甚至还可以用于现代仿制赝品的鉴别。最后，通过对比越窑（南方浙江）和耀州窑（北方陕西）青瓷的瓷胎和瓷釉元素组成，我们还探索了中国南方与北方青瓷的陶瓷原料以及烧制工艺的差异。

3、三维元素分布分析

该部分工作基于前面的深度分析和二维成像，并采用同样的技术——低压氦气辅助高功率飞秒激光电离飞行时间质谱建立了三维成像系统。首先我们利用该系统对自制的四种高纯金属粉末（Cr、Fe、Ni 和 Cu）混合压片样品进行 3D 元素成像，并获得了 50 μm 的横向分辨率和 7 μm 的深度分辨率，验证了该方法的可行性；之后，我们又将其应用于南丹铁陨石的 3D 元素成像，并获得 10^{-6} g/g 的检出限和 6 个数量级的动态范围。对陨石中的亲铁元素（Ni 和 Co）、亲硫元素（Cu、Cr、V 和 Mn）和亲石元素（Li、Na、Mg、Al、K、Ca 和 Ti）的三维空间分布研究发现，亲铁元素主要富集于金属相中，亲硫元素富集于硫化物中，而亲石元素以硅酸盐包容物形式嵌在金属相中；另外在我们分析的立方体中三个非金属元素 S、P 和 C 是聚集在一起的。由这些元素的 3D 空间分布辅助探索了陨石的形成及演化。

关键词： 激光电离；飞行时间质谱；深度分析；二维元素成像；三维元素成像

Abstract

With the rapid development of material science, the traditional solution-based analytical strategy is difficult to satisfy the requirement of modern science, which is attributed to its shortcomings, such as tedious pretreatment for sample, ease to be contaminated, limited capability to get rough composition information etc. Considering these, developing a method with the capacity to directly analyze the solids is receiving increasing interest in analytical chemistry.

An in-house-built buffer-gas assisted high irradiance laser ionization time-of-flight mass spectrometry (LI-TOFMS) has been proved to be an excellent technique for direct solids analysis. Its application fields include conductive sample, semi-conductive and nonconductive one. And it is able to rapidly determine almost all elements simultaneously, including non-metal elements. Moreover, it is capable of performing semi-quantitative analysis without the requirement of calibration by standards, which is vital within the direct solids analysis due to the rarity of matrix matched solid standards. In this dissertation, the study of the composition spatial distribution on the actual solids, which includes one-dimensional, two-dimensional and three-dimensional elemental distribution analysis were performed using LI-TOFMS. The brief introduction of these three sections were demonstrated as follows:

1. One-dimensional elemental distribution analysis

This sectional study demonstrates that the homogeneous crater and uniform ablation is vital for the depth profiling of coating, which can be achieved by a beam expander and an aperture. Firstly, the depth profile of single layer and multilayer samples was carried out by nanosecond laser ionization time-of-flight mass spectrometry (ns-LI-TOFMS). But both of the average ablation rate ($AAR(Zn) = 1.3 \mu\text{m}/\text{pulse}$) and the depth resolution ($\Delta Z(Zn) = 2.4 \mu\text{m}$) were in the range of micrometer. In order to further improve the ability of the technique in the depth profiling, a femtosecond laser

was introduced to compare with the nanosecond laser. The compared results indicate both the average ablation rate ($AAR(Pd) = 55 \text{ nm/pulse}$) and depth resolution ($\Delta Z(Pd) = 310 \text{ nm}$) by fs-LI-TOFMS were one order of magnitude better than ns-LI-TOFMS. Moreover, not only the conductive coating but also the nonconductive one can be analyzed.

2. Two-dimensional elemental distribution analysis

This sectional study demonstrates the capacity of two-dimensional imaging basing on buffer-gas assisted high irradiance femtosecond laser ionization time-of-flight mass spectrometry (fs-LI-TOFMS). The 2D mapping on the cross-section of the ancient celadon, present by elemental distribution in glaze-transition-porcelain body, was carried out to explore the formation mechanism of the transition layer between porcelain body and glaze. Additionally, the composition characteristics of the porcelain body as well as glaze from Yue kiln in different cultural eras (Tang Dynasty, Five Dynasties, Song Dynasty and contemporary era) were revealed. 29 elements in the porcelain body and 25 elements in the glaze were detected. The elements Fe and Ti of porcelain body and Ca, P, Mn and Mg of glaze were considered as characteristic elements to classify the porcelain among different cultural eras, even for the discrimination of the counterfeits from contemporary era. Moreover, elemental composition of celadon body and glaze from the Yue kiln and Yaozhou kiln were compared for further exploring the raw material and firing technologies of porcelain between Southern and Northern kiln.

3. Three-dimensional elemental distribution analysis

This sectional study combines the two previous works, depth profiling and 2D imaging, and develops the ability of three-dimensional imaging using fs-LI-TOFMS. A self-prepared disc mixing four high purity metal powders of Cr, Fe, Ni and Cu, was first introduced to validate the feasibility of the 3D imaging by this technique with a lateral resolution of $50 \mu\text{m}$ and a depth resolution of $7 \mu\text{m}$. Then, 3D imaging was performed on the Nantan meteorite with a detection limit of 10^{-6} g/g and a dynamic range of 6

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