Notice

DESCRIPTION CN120589728A

A method for extracting germanium from germanium-containing lignite and simultaneously preparing hard carbon materials

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一种从含锗褐煤中提取锗同步制备硬碳材料的方法

[0001]

Technical Field

技术领域

[n0001]

This invention relates to a method for efficiently extracting germanium from germanium-containing lignite and simultaneously preparing hard carbon materials, belonging to the fields of metallurgy and materials synthesis technology.

本发明涉及一种从含锗褐煤中高效提取锗同步制备硬碳材料的方法，属于冶金和材料合成技术领域。

[0003]

Background Technology

背景技术

[n0002]

Germanium is a key metal with wide applications in high-tech fields such as infrared optics, fiber optic communication, new energy, and semiconductor materials.

锗是关键金属，在红外光学、光纤通信、新能源和半导体材料等高新技术领域有着广泛的应用。

As a new wave of artificial intelligence sweeps the globe, the demand for high-end chips is experiencing explosive growth, and germanium, as a key raw material for chip manufacturing, occupies a pivotal position.

随着新一轮人工智能浪潮席卷全球，高端芯片需求量呈现爆发式增长，锗作为芯片制造的关键原料占据举足轻重的地位。

Developed Western countries such as the United States, the European Union, and Japan have enacted critical mineral laws to strictly control germanium in order to maintain their advantage in cutting-edge technology fields.

美国、欧盟和日本等西方发达国家纷纷通过制定关键矿产法案对锗进行严格控制，以维护其在尖端科技领域的优势。

The struggle for control of germanium has become a new focal point in the great power resource game. Germanium resources are of great significance for ensuring national resource security, promoting the development of high-tech industries, and occupying new high ground in the great power resource game.

锗的控制权争夺已然成为大国资源博弈的新焦点，锗资源对于保障国家资源安全、推动高新技术产业发展、占领大国资源博弈新高地具有重要的意义。

[n0003]

Germanium-bearing lignite accounts for about half of my country's germanium reserves and is an important source for the development and utilization of germanium resources in my country.

含锗褐煤占我国锗储量的一半左右，是当前我国锗资源开发利用的重要来源。

The existing lignite germanium extraction process uses a crude method of combustion enrichment-chlorination distillation, which faces multiple challenges such as low germanium recovery rate, high consumption of auxiliary materials, and difficulty in treating waste acid and waste residue. Germanium enrichment through lignite combustion involves burning lignite in a chain grate furnace (~1000°C) or a vortex furnace (>1200°C) at even higher temperatures. By controlling the atmosphere in the furnace to be a weak reducing atmosphere, germanium is reduced to GeO, volatilized, and enriched in the flue gas. However, existing methods for enriching germanium through the combustion of lignite have significant problems, such as low germanium volatilization efficiency and low germanium grade in germanium-containing flue dust.

现有褐煤提锗采用燃烧富集-氯化蒸馏的粗放型工艺，面临锗回收率低、辅料消耗大、废酸废渣难处理等多重挑战。 褐煤燃烧富集锗是将褐煤在链条炉(～1000°C)或温度更高的漩涡炉(>1200°C)中燃烧，通过控制炉中气氛为弱还原气氛，将锗还原为GeO形态挥发并在烟尘中富集。 然而，现有褐煤燃烧富集锗存在锗挥发效率低、含锗烟尘中锗品位低等显著问题。

[n0004]

Hard carbon is a material that is difficult to graphitize. It has advantages such as high stability, stable performance, low cost, and high reversible capacity, making it a popular research target for sodium-ion battery anode materials.

硬碳是一种难以被石墨化的材料，具有稳定性高、性能稳定、成本低、可逆容量高等优点，成为钠离子电池负极材料的热门研究对象。

Currently, the precursors for the preparation of hard carbon materials mainly include biomass, resin-based, petroleum-based, and coal-based raw materials. Among them, coal-based raw materials have advantages such as wide availability, low cost, and sustainability, and are gradually attracting the attention of researchers. The preparation methods of hard carbon materials include direct carbonization, hydrothermal carbonization, physical or chemical activation, etc., but they generally have significant problems such as long carbonization time, low efficiency and high energy consumption.

当前，硬碳材料制备的前驱体主要包括生物质、树脂基、石油基和煤基原料，其中煤基原料具有来源广泛、成本低、可持续性等优点，逐渐引起研究者们的关注。 硬碳材料的制备方法包括：直接碳化、水热碳化、物理或化学活化等，但普遍存在碳化时间长、效率低、能耗高等显著问题。

[n0005]

In view of the current problems in germanium extraction from germanium-containing lignite and the characteristics of rapid material preparation by Joule heating, we have innovatively developed a new method for extracting germanium from germanium-containing lignite and simultaneously preparing hard carbon materials.

鉴于目前含锗褐煤提锗存在的问题以及焦耳热快速制备材料的特点，我们创新地开发了一种从含锗褐煤中提取锗同步制备硬碳材料的新方法。

It can not only achieve efficient extraction of germanium from lignite, but also synthesize high-value hard carbon materials from low-quality lignite. There have been no related reports yet.

不仅能够实现褐煤中锗的高效提取，同时能够将劣质的褐煤合成高价值的硬碳材料。 目前还未见相关报道。

[0008]

Summary of the Invention

发明内容

[n0006]

This invention aims to provide a method for efficiently extracting germanium from germanium-containing lignite and simultaneously preparing hard carbon materials.

本发明旨在提供一种从含锗褐煤中高效提取锗同步制备硬碳材料的方法。

Germanium-containing lignite is placed in a flash Joule heating device and rapidly heated to 500-3000°C by applying an electric current to generate Joule heat under vacuum or protective atmosphere for 0.1-10s. Then it is rapidly cooled to room temperature. This heating-cooling process is repeated several times to obtain germanium-rich sublimes and pyrolysis residues. The residues are then acid-leached and filtered to obtain hard carbon materials.

将含锗褐煤置于闪蒸焦耳热设备中，在真空或保护气氛下通过施加电流产生焦耳热的方式快速升温至500-3000°C，施加电流时间为0.1-10s，然后迅速降至室温，该升温-降温程序循环数次，分别得到富锗凝华物和热解残留物，残留物经酸浸过滤后获得硬碳材料。

This invention has significant advantages such as high germanium extraction efficiency and high product value.

本发明具有锗提取效率高、产品价值高等显著优点。

[n0007]

A method for extracting germanium from germanium-containing lignite and simultaneously preparing hard carbon materials includes the following steps:

一种从含锗褐煤中提取锗同步制备硬碳材料的方法，包括以下步骤：

[n0008]

Step 1: Place germanium-containing lignite in a Joule heating device and rapidly heat it to 500-3000°C by applying an electric current to generate Joule heat under vacuum or protective atmosphere. The current application time is 0.1-10s. Then cool it down to room temperature. Repeat this heating-cooling process several times to obtain germanium-rich sublimes and pyrolysis residues.

步骤1：将含锗褐煤置于焦耳热设备中，在真空或保护气氛下通过施加电流产生焦耳热的方式快速升温至500-3000°C，施加电流时间为0.1-10s，然后降至室温，该升温-降温程序循环数次，分别得到富锗凝华物和热解残留物；

[n0009]

Step 2: Mix the pyrolysis residue obtained in Step 1 with acid for leaching. After the reaction is completed, obtain hard carbon material by solid-liquid separation.

步骤2：将步骤1所得热解残留物和酸进行混合浸出，反应结束后经固液分离获得硬碳材料。

[n0010]

In step 1, the germanium-containing lignite used has a particle size of 100% less than 74 μm.

步骤1中，所用的含锗褐煤粒度100%小于74μm。

[n0011]

In step 1, the heating environment is a vacuum or a protective atmosphere, wherein the protective atmosphere includes: N₂, Ar or O₂.

步骤1中，加热环境为真空或保护气氛，其中保护性气氛包括：N₂、Ar或O₂。

[n0012]

In step 1, the applied current is a pulse current, alternating current, constant current, decaying current, or a combination of the above.

步骤1中，所施加的电流为脉冲电流、交变电流、恒定电流、衰减电流或以上电流组合。

[n0013]

In step 1, the applied current intensity is 100-150A, the duration is 0.1-10s, and the peak temperature is 500-3000°C.

步骤1中，施加电流强度为100-150A，持续时间为0.1-10s，峰值温度为500-3000°C。

[n0014]

In step 1, the heating rate is 10³-10⁴°C/s, the cooling rate is 10²-10³°C/s, and the heating-cooling program cycle number is 1-20 times.

步骤1中，升温速率为10³-10⁴°C/s，降温速率为10²-10³°C/s，升温-降温程序循环次数为1-20次。

[n0015]

In step 2, the acid used is one or a combination of hydrochloric acid, sulfuric acid, nitric acid, and hydrofluoric acid, and the concentration of the acid is 10-15%.

步骤2中，所用的酸为盐酸、硫酸、硝酸、氢氟酸中的一种或组合，酸的浓度为10～15%。

[n0016]

In step 2, the pickling temperature is 20-90°C, the pickling time is 10-60min, and the liquid-to-solid ratio is 1-10mL/g.

步骤2中，酸洗的温度为20-90°C，酸洗时间为10-60min，液固比为1-10mL/g。

[n0017]

The main chemical reaction equations of this invention are as follows:

本发明的主要化学反应方程式如下:

[n0018]

GeO₂(s)+C(s)=GeO(g)+CO(g)

GeO₂(s)+C(s)＝GeO(g)+CO(g)

[n0019]

GeO₂(s)+CO(g)=GeO(g)+CO₂(g)

GeO₂(s)+CO(g)＝GeO(g)+CO₂(g)

[n0020]

GeO₂(s)+H₂(g)=GeO(g)+H₂O(g)

GeO₂(s)+H₂(g)＝GeO(g)+H₂O(g)

[n0021]

GeO₂(s)+H₂S(g)=GeS(g)+H₂O(g)

GeO₂(s)+H₂S(g)＝GeS(g)+H₂O(g)

[n0022]

CaO(s)+2H⁺(aq)=Ca²⁺(aq)+H₂O(l)

CaO(s)+2H⁺(aq)＝Ca²⁺(aq)+H₂O(l)

[n0023]

MgO(s)+2H⁺(aq)=Mg²⁺(aq)+H₂O(l)

MgO(s)+2H⁺(aq)＝Mg²⁺(aq)+H₂O(l)

[n0024]

Al₂O₃(s)+6H⁺(aq)＝2Al³⁺(aq)+3H<sub>2<

/sub>O(l)

Al₂O₃(s)+6H⁺(aq)＝2Al³⁺(aq)+3H<sub>2<

/sub>O(l)

[n0025]

Fe₂O₃(s)+6H⁺(aq)＝2Fe³⁺(aq)+3H<sub>2<

/sub>O(l)

Fe₂O₃(s)+6H⁺(aq)＝2Fe³⁺(aq)+3H₂O(l)

[n0026]

The working principle of this invention is as follows: Germanium-containing lignite is pyrolyzed under Joule thermal shock. During the pyrolysis process, germanium is transformed into GeO or GeS. Since GeO and GeS have high saturated vapor pressure, they are vaporized and volatilized at high temperature. Germanium-rich products are obtained by collecting the condensate.

本发明的作用原理在于：含锗褐煤在焦耳热冲击下进行热解，热解过程中，锗转变为GeO或GeS，由于GeO和GeS的饱和蒸气压较大，在高温下变成蒸汽挥发出去，通过收集冷凝物获得富锗产品。

At high temperatures, the carbon components in lignite undergo carbonization. During the carbonization process, some carbon elements are oxidized and volatilized, releasing small molecule gases such as CH₄, CO₂, and H₂, which causes a large number of micropores to form on the material surface.

高温下褐煤中的碳组分在高温下进行碳化，碳化的过程中伴随着部分碳元素的氧化和挥发，会释放一些小分子气体如CH₄、CO₂、H₂等，使得材料表明产生大量微孔。

Simultaneously, carbon atoms rearrange themselves, undergoing aromatization and condensation reactions, thereby generating structurally stable carbon grid units. These carbon grid units stack randomly and disorderly, eventually forming hard carbon.

同时碳原子进行重排，相继发生芳构化、缩聚反应，由此生成结构稳定的碳网格单元，这些碳网格单元杂乱无序的堆叠，最终形成硬碳。

Because lignite usually contains some inorganic minerals (CaO, MgO, Al35O36, Fe37O38, etc.), ash is formed during pyrolysis.

由于褐煤中通常含有一部分的无机质矿物(CaO、MgO、Al₂O₃、Fe₂O₃等)，在热解的过程中形成灰分。

The inorganic minerals can be removed from the pyrolysis products by acid leaching, thus obtaining hard carbon materials.

将热解的产物通过酸浸可以脱出无机质矿物，从而得到硬碳材料。

[n0027]

The beneficial effects of this invention are as follows:

本发明的有益效果为：

[n0028]

Compared with existing methods for enriching germanium by burning lignite, this invention can not only quickly separate and enrich germanium, but also avoid the waste of carbon components caused by burning lignite and synthesize high-value carbon materials.

相较于现有褐煤燃烧富集锗的方法，本发明不仅能快速实现锗的分离与富集，而且避免了褐煤燃烧造成碳组分的浪费且合成高价值的碳材料。

This provides a new approach for the efficient and comprehensive utilization of germanium-containing lignite.

为含锗褐煤的高效综合利用提供了新的利用途径。

[0032]

Detailed Implementation

具体实施方式

[n0029]

The present invention will be further described below with reference to specific embodiments, but the scope of protection of the present invention is not limited thereto.

下面结合及具体实施例对本发明作进一步的说明，但本发明的保护范围并不限于此。

[n0030]

Example 1

实施例1

[n0031]

0.5g of germanium-containing lignite was placed in a flash Joule heating apparatus for thermal shock. The pyrolysis environment was an Ar atmosphere, the applied current was 120A, the applied current time was 800ms, the peak temperature was 1500°C, and the heating-cooling program was repeated 10 times. The sublimation and pyrolysis residue were collected separately.

将0.5g含锗褐煤置于闪蒸焦耳热设备中进行热冲击，热解环境为Ar气气氛，施加电流为120A，施加电流时间为800ms，峰值温度为1500℃，升温-降温程序循环次数为10次，分别收集凝华物和热解残渣。

The volatilization rate of germanium was calculated by chemical analysis of the condensate. The pyrolysis residue was leached with 10% hydrochloric acid at a solid-liquid ratio of 1:10 at 80°C for 30 minutes. Hard carbon material was obtained by solid-liquid separation.

凝华物经化验分析计算锗的挥发率，热解残渣与10%浓度的盐酸按照1:10的固液比在80℃浸出30min，经固液分离获得硬碳材料。

[n0032]

In this Example 1, the volatility of germanium was 98.2%, the yield of hard carbon material was 45.6%, and the carbon content was 95.9%.

本实施例1中，锗的挥发率为98.2%，硬碳材料的产率为45.6%，碳含量为95.9%。

[n0033]

Example 2

实施例2

[n0034]

0.5g of germanium-containing lignite was placed in a flash Joule heating apparatus for thermal shock. The pyrolysis environment was an Ar atmosphere, the applied current was 100A, the applied current time was 500ms, the peak temperature was 1200°C, and the heating-cooling program was repeated 5 times. The sublimation and pyrolysis residue were collected separately.

将0.5g含锗褐煤置于闪蒸焦耳热设备中进行热冲击，热解环境为Ar气气氛，施加电流为100A，施加电流时间为500ms，峰值温度为1200°C，升温-降温程序循环次数为5次，分别收集凝华物和热解残渣。

The volatilization rate of germanium was calculated by chemical analysis of the condensate. The pyrolysis residue was leached with 10% hydrochloric acid at a solid-liquid ratio of 1:10 at 80°C for 30 minutes. Hard carbon material was obtained by solid-liquid separation.

凝华物经化验分析计算锗的挥发率，热解残渣与10%浓度的盐酸按照1:10的固液比在80°C浸出30min，经固液分离获得硬碳材料。

[n0035]

In this Example 2, the volatility of germanium was 84.6%, the yield of hard carbon material was 57.9%, and the carbon content was 90.3%.

本实施例2中，锗的挥发率为84.6%，硬碳材料的产率为57.9%，碳含量为90.3%。

[n0036]

Example 3

实施例3

[n0037]

0.5g of germanium-containing lignite was placed in a flash Joule heating apparatus for thermal shock. The pyrolysis environment was an Ar atmosphere, the applied current was 130A, the applied current time was 100ms, the peak temperature was 1600°C, and the heating-cooling program cycle was 1 time. The sublimation and pyrolysis residue were collected separately.

将0.5g含锗褐煤置于闪蒸焦耳热设备中进行热冲击，热解环境为Ar气气氛，施加电流为130A，施加电流时间为100ms，峰值温度为1600℃，升温-降温程序循环次数为1次，分别收集凝华物和热解残渣。

The volatilization rate of germanium was calculated by chemical analysis of the condensate. The pyrolysis residue was leached with 10% hydrochloric acid at a solid-liquid ratio of 1:10 at 80°C for 30 minutes. Hard carbon material was obtained by solid-liquid separation.

凝华物经化验分析计算锗的挥发率，热解残渣与10%浓度的盐酸按照1:10的固液比在80℃浸出30min，经固液分离获得硬碳材料。

[n0038]

In this Example 3, the volatility of germanium was 61.8%, the yield of hard carbon material was 51.6%, and the carbon content was 92.7%.

本实施例3中，锗的挥发率为61.8%，硬碳材料的产率为51.6%，碳含量为92.7%。

[n0039]

Example 4

实施例4

[n0040]

0.5g of germanium-containing lignite was placed in a flash Joule heating apparatus for thermal shock. The pyrolysis environment was an Ar atmosphere, the applied current was 110A, the applied current time was 800ms, the peak temperature was 1400°C, and the heating-cooling program cycle was 20 times. The sublimation and pyrolysis residue were collected separately.

将0.5g含锗褐煤置于闪蒸焦耳热设备中进行热冲击，热解环境为Ar气气氛，施加电流为110A，施加电流时间为800ms，峰值温度为1400°C，升温-降温程序循环次数为20次，分别收集凝华物和热解残渣。

The volatilization rate of germanium was calculated by chemical analysis of the condensate. The pyrolysis residue was leached with 10% sulfuric acid and hydrofluoric acid at a solid-liquid ratio of 1:10 at 80°C for 30 minutes. Hard carbon material was obtained by solid-liquid separation.

凝华物经化验分析计算锗的挥发率，热解残渣与10%浓度的硫酸和氢氟酸按照1:10的固液比在80°C浸出30min，经固液分离获得硬碳材料。

[n0041]

In this Example 4, the volatility of germanium was 98.5%, the yield of hard carbon material was 41.3%, and the carbon content was 98.2%.

本实施例4中，锗的挥发率为98.5%，硬碳材料的产率为41.3%，碳含量为98.2%。

[n0042]

Example 5

实施例5

[n0043]

0.5g of germanium-containing lignite was placed in a flash Joule heating apparatus for thermal shock. The pyrolysis environment was O₂ atmosphere, the applied current was 120A, the applied current time was 500ms, the peak temperature was 1500°C, and the heating-cooling program cycle was 20 times. The sublimation and pyrolysis residue were collected separately.

将0.5g含锗褐煤置于闪蒸焦耳热设备中进行热冲击，热解环境为O₂气氛，施加电流为120A，施加电流时间为500ms，峰值温度为1500℃，升温-降温程序循环次数为20次，分别收集凝华物和热解残渣。

The volatilization rate of germanium was calculated by chemical analysis of the condensate. The pyrolysis residue was leached with 10% sulfuric acid at a solid-liquid ratio of 1:10 at 80°C for 30 minutes. Hard carbon material was obtained by solid-liquid separation.

凝华物经化验分析计算锗的挥发率，热解残渣与10%浓度的硫酸按照1:10的固液比在80℃浸出30min，经固液分离获得硬碳材料。

[n0044]

In this Example 5, the volatility of germanium was 98.9%, the yield of hard carbon material was 30.4%, and the carbon content was 85.1%.

本实施例5中，锗的挥发率为98.9%，硬碳材料的产率为30.4%，碳含量为85.1%。

[n0045]

Example 6

实施例6

[n0046]

0.5g of germanium-containing lignite was placed in a flash Joule heating apparatus for thermal shock. The pyrolysis environment was O₂ atmosphere, the applied current was 150A, the applied current time was 500ms, the peak temperature was 2000℃, and the heating-cooling program cycle was 10 times. The sublimation and pyrolysis residue were collected separately.

将0.5g含锗褐煤置于闪蒸焦耳热设备中进行热冲击，热解环境为O₂气氛，施加电流为150A，施加电流时间为500ms，峰值温度为2000℃，升温-降温程序循环次数为10次，分别收集凝华物和热解残渣。

The volatilization rate of germanium was calculated by chemical analysis of the condensate. The pyrolysis residue was leached with 10% sulfuric acid and hydrofluoric acid at a solid-liquid ratio of 1:10 at 80°C for 30 minutes. Hard carbon material was obtained by solid-liquid separation.

凝华物经化验分析计算锗的挥发率，热解残渣与10%浓度的硫酸和氢氟酸按照1:10的固液比在80℃浸出30min，经固液分离获得硬碳材料。

[n0047]

In this Example 6, the volatilization rate of germanium was 98.5%, the yield of hard carbon material was 35.1%, and the carbon content was 88.7%.

本实施例6中，锗的挥发率为98.5%，硬碳材料的产率为35.1%，碳含量为88.7%。